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ON THE IRREGULARITY OF THE Kα DOUBLETS IN THE ELEMENTS OF LOWER ATOMIC NUMBERS

By D. M. Bose

Abstract

In this paper attention is drawn to the recent measurements of the separation $\Delta\lambda$ of the Kα doublets of the lighter elements from Al(13) to Ge(32) by Siegbahn and Ray and by Bäcklin. From these measurements it appears that the experimentally determined values of $\Delta\nu/R(Z-3.5)^4$ deviate systematically from those calculated according to the relativity formula of Sommerfeld. This deviation is especially large in the case of the Fe group of elements. In order to account for this deviation it is supposed that the experimentally determined $\Delta\nu/R=\Delta\nu_{rel}/R+\Delta\nu_{mag}/R$. The first term on the right hand side is due to the relativity change in the mass of the radiating electron in the two orbits which produce the relativity doublet, and which can be calculated according to Sommerfeld's formula. The second term is due to the difference in the magnetic energy of the excited atom corresponding to the two different k_2 values of the radiating electron. To calculate this term use has been made of the model which was proposed by Landé to explain the relativity doublet on a magnetic basis. According to the calculations it is shown that $\Delta\nu_{mag}/R(Z-3.5)^3=\alpha^2/14$ or $3\alpha^2/32$ according to the interpretation which is given to k_2. The first formula is obtained if k_2 determines the inclination of the orbit of the radiating electron, while the second formula is obtained if k_2 determines the shape of the electron orbit. The mean of the experimentally calculated values agrees better with the second formula.

The peculiar behavior of the $K\alpha$ doublets belonging to the first transition group of elements is accounted for on the assumption that the inner magnetic fields in the atoms of these elements are large and therefore produce greater magnetic separation. It is further shown that the hypothesis, that the M_{32} sub-level is formed first in this group of elements, and then the M_{31} sub-level, which was introduced in a previous paper to explain the paramagnetic moments of these elements, receive further support from the above mentioned data.

RECENTLY the separation $\Delta\lambda$ of the Kα doublets of the lighter elements has been the object of accurate measurements by Siegbahn and Ray,[1] and by Bäcklin.[2] In Table 1, column 2, the values of $\Delta\lambda$ for the Kα doublets of the elements Al(13) to K (18) have been taken from Bäcklin and of the elements Ca(20) to Ge(32) from Siegbahn and Ray. With these values of $\Delta\lambda$ I have calculated in column 4 the values

[1] Siegbahn and Ray, Ark. f. Mat. Asts. O. Fys. **18**, 1 (1924).
[2] Bäcklin, Zeits. f. Physik **33**, 547 (1925).

of $\Delta\nu/R(Z-3.5)^4$ for these elements and plotted them in curve II of Fig. 1. In curve I have been plotted the values of the same quantity as calculated according to Sommerfeld's relativity formula

$$\frac{\Delta\nu}{R(Z-3.5)^4} = \frac{\alpha^2}{2^4}\left[1+\frac{5}{2}(Z-3.5)^2+\cdots\right]$$

It will be seen that the difference between these two sets of values of $\Delta\nu/R(Z-3.5)^4$ for different values of Z decreases continuously with increasing Z, with a sudden rise and subsequent fall as we pass along the transition groups of elements. It is the purpose of the present paper to offer an explanation of this deviation of the experimentally deter-

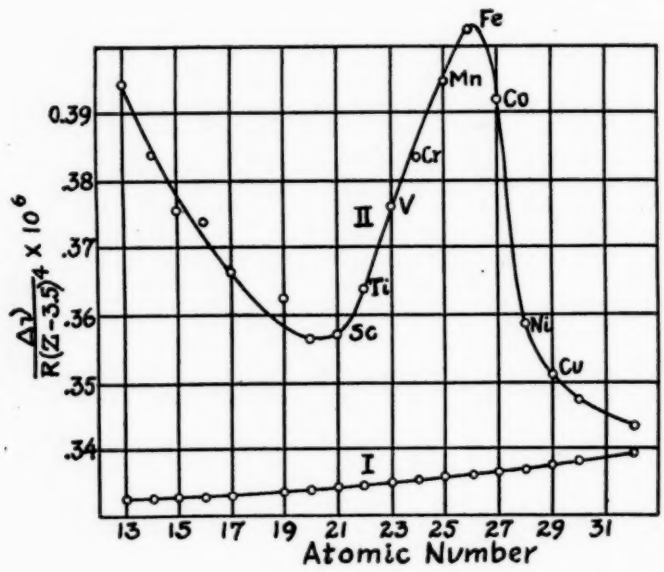

FIG. 1

mined values of $\Delta\nu/R(Z-3.5)^4$ from those calculated according to Sommerfeld's formula. The explanation is based on the assumption that the difference in energy radiated by the emitting atom in the two states corresponding to the two orbits of the radiating electron is due, not only to the relativity change of mass of the latter but also to the change in the magnetic energy of the atom in these two states.

We shall deal first with the continuous decrease in the value of $(\Delta\nu_{obs}-\Delta\nu_{cal})/R(Z-3.5)^4$ with increase of Z, and then we shall consider the anomalous behavior of the Kα doublets of the elements Sc (21) to Cu (29).

I. Continuous Decrease of $(\Delta\nu_{obs}-\Delta\nu_{rel})/R(Z-3.5)^4$ with Increase of Z

The x-ray energy levels are characterized according to the notation introduced by Bohr and Coster[3] by three quantum numbers $n(k_1k_2)$, where k_1 and k_2 are the two azimuthal quantum numbers such that $k_2=k_1$ or k_1-1. The rules governing their transitions are $k_1\rightarrow k_1\pm 1$ and $k_2\rightarrow k_2\pm 1$ or k_2. In the optical spectra any one term is represented by n_{kj}, and from the rules governing the transition of k and j it can be shown that k_1 is similar to the azimuthal quantum number k and k_2 to the inner quantum number j. This similarity between x-ray and optical doublet terms has been pointed out by Landé.[4] According to the then accepted theory of the magnetic origin of optical doublets, Landé has in this paper proposed a similar explanation of these so-called relativity Kα doublets. He supposes that in an atom in which every shell has received its maximum number of electrons, the resultant moment of each is vanishingly small except in the case of the K-shell which has a resultant of one Bohr's unit of $h/2\pi$. If now from any shell containing say $2n$ electrons with the azimuthal number k one is ejected, then the remaining $2n-1$ electrons break up into a stable configuration of $2n-2$ electrons with resultant moment equal to zero, and a radiating electron with azimuthal number k. The vectorial addition of the unit moment of the atom core (K-shell) and the moment k of the radiating electron can give rise to two values of atomic moment j, viz., k and $k-1$. If we identify k_1 with k and k_2 with j we get at once an explanation of the doublet nature of the x-ray terms.

Two energy levels for which n and k_1 are the same and k_2 differs by unity form a relativity doublet. This would imply according to Landé that the atom core has two different inclinations with respect to the orbit of the radiating electron, and the term difference $\Delta\nu_{mag}$ can be calculated, according to a model proposed by Heisenberg, as follows

$$\Delta\nu_{mag}=\overline{H}o\Delta m/2\pi \qquad (1)$$

where $\overline{H}=32\pi^5m^2e^7Z^3/ch^5n^3k^2$ is the average field created by the radiating electron, and o is Larmor's precession in unit magnetic field. Δm is the change in the quantum number of the atom core, resolved parallel to the direction of $\overline{H}$.

[3] Bohr and Coster, Zeits. f. Physik **12**, 342 (1923).

[4] Landé, Zeits. f. Physik **24**, 88 (1924).

On substituting these values in (1) we get

$$\Delta\nu_{mag}=\frac{8\pi^4me^8}{h^5c^2n^3k^2}Z^3\Delta m$$

$$=\frac{R\alpha^2}{n^3k^2}Z^3\Delta m$$

since

$$R=2\pi^2me^4/h^3 \text{ and } \alpha^2=4\pi^2e^4/h^2c^2 .$$

If we take into account the screening effect, then

$$\Delta\nu_{mag}/R(Z-3.5)^3=\alpha^2/n^3k^2 . \tag{3a}$$

We get another expression for $\Delta\nu_{mag}$ if we assume, as is necessary to explain the origin of these doublets on the relativity theory, that k_2 is the azimuthal quantum number, so that a change in k_2 represents an alteration in the shape of the orbit of the radiating electron and not in its inclination. In this case if m is the equatorial quantum number of the atom in the direction of $\overline{H}$, then the magnetic energy of the former in the field of the radiating electron is

$$\Delta E_{kin}=moL\overline{H}/2\pi$$

Keeping m constant and altering k_2, i.e. $\overline{H}$, we get

$$\Delta\nu_{mag}=\frac{\Delta E_{kin}^{(1)}-\Delta E_{kin}^{(2)}}{h}$$

$$=\frac{R\alpha^2(Z-3.5)^3m}{n^3}\left(\frac{1}{k_2'^2}-\frac{1}{k_2''^2}\right)$$

or

$$\frac{\Delta\nu_{mag}}{R(Z-3.5)^3}=\frac{\alpha^2m}{n^3}\left(\frac{1}{k_2'^2}-\frac{1}{k_2''^2}\right) . \tag{3b}$$

The corresponding expression for the relativity separation is

$$\frac{\Delta\nu_{rel}}{R(Z-3.5)^4}=\frac{\alpha_2(k_2''-k_2')}{n^3k_2'k_2''} \tag{4}$$

In the case of the Kα doublet $k_2'=1$; $k_2''=2$ while the value of k^2 in (3a) is according to Landé equal to $k^2-\frac{1}{4}=7/4$. Further in (3a) $\Delta m=1$ and in (3b) $m=1$.

Then according to (3a)

$$\Delta\nu_{mag}/R(Z-3.5)^3=\alpha^2/14 \tag{5a}$$

and according to (3b)

$$\Delta\nu_{mag}/R(Z-3.5)^3=3\alpha^2/32\ . \tag{5b}$$

From (4)

$$\Delta\nu_{rel}/R(Z-3.5)^4=\alpha^2/16\ . \tag{6}$$

The formulas (3a) and (3b) have been deduced on the assumption that the magnetic energy is due entirely to the action between the magnetic moment of the K-shell and the field due to the radiating electron. If in addition there are other shells with uncompensated magnetic moments there will then be further addition to the magnetic energy of the excited atom. This term is at present difficult to calculate.

The burden of the experimental evidence is in favor of Sommerfeld's relativity formula, and Landé himself has given up his views about the magnetic origin of the Röntgen doublets. There is no reason however to suppose that the two effects cannot exist side by side, so that the observed separation $\Delta\nu_{obs}/R$ can be represented as being given by

$$\begin{aligned}\frac{\Delta\nu_{obs}}{R}&=\frac{\Delta\nu_{rel}}{R}+\frac{\Delta\nu_{mag}}{R}\\&=(Z-3.5)^4\frac{\alpha^2}{16}\left(1+\frac{16}{14}\,\frac{1}{Z-3.5}\right)\text{ according to (5a)}\\&=(Z-3.5)^4\frac{\alpha^2}{16}\left(1+\frac{3}{2}\,\frac{1}{Z-3.5}\right)\text{ according to (5b)}\end{aligned}$$

For large values of Z, the second term on the right hand side is negligible in comparison to the first, and it is in this region that Sommerfeld's formula has been so well experimentally verified. While for small values of Z, i.e., in the region studied by Siegbahn and Ray and by Bäcklin, the second term is no longer negligible, and we have then, according to (5a),

$$\frac{\Delta\nu_{obs}-\Delta\nu_{rel}}{R(Z-3.5)^3}=\frac{\Delta\nu_{mag}}{R(Z-3.5)^3}=\frac{\alpha^2}{14}=\frac{5.31\times10^{-5}}{14}=3.8\times10^{-6}$$

and according to (5b) the same expression has the value $3\alpha^2/32$ or 4.97×10^{-6}

In Table I, I have subtracted from the observed values of $\Delta\nu/R$, the values of $\Delta\nu_{rel}/R$ calculated according to Sommerfeld's formula, and have called these differences $\Delta\nu_{mag}/R$. According to the view that is taken of the azimuthal quantum number k_2, the value of $\Delta\nu_{mag}/R(Z-3.5)^3$ ought to be either 3.8×10^{-6} or 4.97×10^{-6}.

In column VII, I have placed the calculated values of this quantity for the elements Al(13) to Ge(32). Leaving for the present the transition group of elements Sc(21) to Cu(29), we find that with the exception of the very low value for Zn(30) the other elements give values for this quantity of the expected magnitude. Omitting Zn, the mean value is found to be 4.78×10^{-6}, which is very near to the value calculated according to 5(b). This would imply that so far as the magnetic energy of the atom is concerned, the second azimuthal quantum number k_2 represents the shape of the orbit of the radiating electron, and not its inclination to the atom core.

TABLE I

Z	$\Delta\lambda$	$\Delta\nu/R$	$\dfrac{\Delta\nu}{R(Z-3.5)^4}$	$\Delta\nu/R$ (rel)	$\Delta\nu/R$ (mag)	$\dfrac{\Delta\nu_{mag}}{R(Z-3.5)^3\times10^6}$
13Al	2.44	0.03139	0.3943	0.02706	0.00433	5.05
14Si	2.58	0.04651	0.3838	0.04037	0.00614	5.32
15P	2.72	0.06570	0.3759	0.05814	0.00756	4.97
16S	2.88	0.09131	0.3742	0.08122	0.01009	5.05
17Cl	2.97	0.12150	0.3660	0.1106	0.0109	4.43
19K	3.21	0.20950	0.3631	0.1925	0.0170	4.57
20Ca	3.26	0.26440	0.3570	0.2475	0.0169	3.76
21Sc	3.37	0.33560	0.3576	0.3136	0.0220	4.11
22Ti	3.45	0.41780	0.3643	0.3920	0.0258	4.07
23V	3.60	0.52550	0.3763	0.4845	0.0410	5.54
24Cr	3.89	0.67900	0.3836	0.6064	0.0726	8.31
25Mn	4.08	0.84500	0.3949	0.7180	0.1270	12.77
26Fe	4.22	1.0250	0.4019	0.8624	0.1626	14.28
27Co	4.19	1.1920	0.3920	1.027	0.1650	12.72
28Ni	3.90	1.2920	0.3588	1.214	0.078	5.30
29Cu	3.86	1.4810	0.3514	1.430	0.051	3.08
30Zn	3.82	1.6890	0.3475	1.670	0.019	1.02
32Ge	3.91	2.2650	0.3439	2.243	0.022	5.09

II. THE ANOMALOUS BEHAVIOR OF THE Kα DOUBLETS OF THE ELEMENTS Sc(21) TO Cu(29)

The view which has been considered above receives further support when we consider the anomalous behavior of the Kα doublets of the transition group of elements which are strongly paramagnetic. According to the scheme of distribution of electrons in the different atomic sub-levels proposed by Stoner,[5] it is supposed that every such sub-level is characterized by the numbers n_{kj}, and the maximum number of electrons which can occupy any one of them is $2j$. In the first transition group of elements from Sc(21) to Cu(29), it is supposed that the two inner 3-quanta sub-levels M_{32} and M_{33} are built up with 4 and 6 elec-

[5] Stoner, Phil. Mag. 48, 719 (1924).

trons respectively. In a previous paper,[6] I have shown that from magnetic evidences it can be concluded that the M_{33} sub-level is first completed at Fe(26) and then the M_{32} sub-level is completed between Co(27) and Cu(29). In order to explain the experimental values of the magneton numbers of the atoms and ions of these elements, it had to be assumed that the M_{32} electrons move in a sense opposite to those of the M_{33} ones. It is at once evident that in the atoms of these elements strong inner magnetic fields exist, and in calculating the magnetic

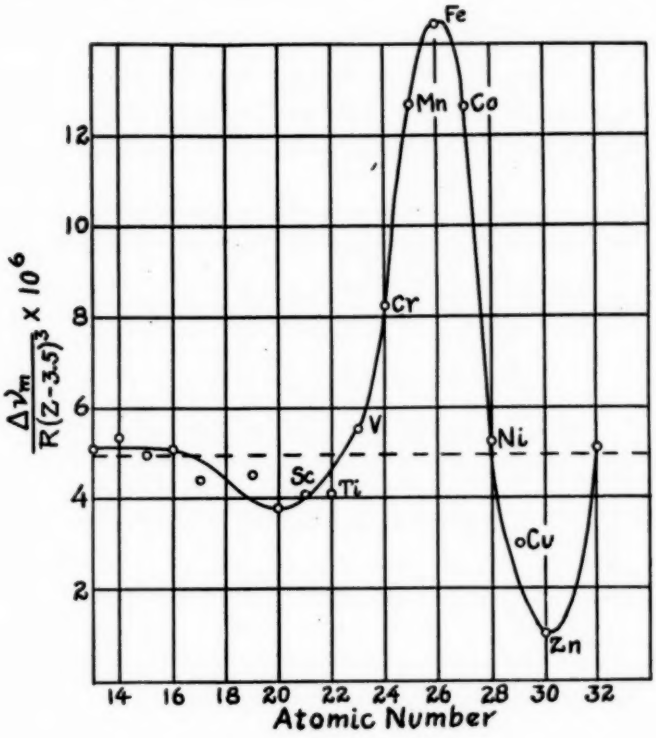

FIG. 2

energy of the excited atom we have to take into consideration not only the energy of the atom core (i.e. of the K-shell) with respect to the magnetic field of the radiating electron, but also of the freshly formed M_{32} and M_{33} shells, and we can see why in these elements the value of $\Delta\nu_{mag}/R$ is large. In Fig. 2, I have plotted the values of $\Delta\nu_{mag}/R(Z-3.5)^3$ as a function of Z, and it will be noticed that the curve bends sharply upwards at Ca(20) and reaches its maximum at Fe(26), and then it bends downwards and reaches a minimum at Zn(30).

[6] Bose, Zeits. f. Physik **35**, 213 (1925).

It seems as if the inner magnetic field reaches its maximum value when M_{33} sub-level is completed at Fe(26), and that this field is gradually neutralized by the one due to the motion of the electrons in the M_{32} orbits. We have thus an independent verification of the successive formation of the M_{33} and M_{32} sub-levels in these elements, a hypothesis which was assumed in a previous paper to explain certain magnetic effects.

Here an interesting question arises as to the resultant value of the magnetic moment of the six electrons in the M_{33} sub-level in the atoms of Fe(26) and the other heavier elements of this group. From spectroscopic evidences Sommerfeld and his co-workers[7] have concluded that the magneton number of Fe, Co, and Ni are 6, 6 and 5 respectively. These values do not at all agree with the values of the atomic moments found by Gerlach[7] for the elements Fe, Ni and Cu, which were found to be 0, 2 and 1 magnetons respectively. In the previous paper,[6] I have tried to calculate the magnetic moments of these elements and their ions from the following distribution of electrons.

	M_{32}	M_{33}	N_{11}
Fe:	–	6	2
Co:	1	6	2
Ni:	2	6	2
Cu:	4	6	1

The assumptions made were (i) that the magneton number is $M_{33}+N_{11}+M_{32}$, (ii) when any sub-level has received its maximum number of $2j$ electrons its resultant moment is zero. On these assumptions the atomic moments of the elements Fe, Ni and Cu come out to be 0, 2 and 1 respectively in agreement with Gerlach's results. On the other hand if we alter (ii) and suppose that the M_{33} sub-level always contributes 6 magnetons to the total moment of the atom, then for the elements Fe, Co and Ni the values of the magneton numbers come out to be 6, 5, 4 respectively which are close enough to the spectroscopically determined values of 6, 6, and 6. In the case of the Kα doublets of these elements, we have similarly to suppose that the magnetic field produced by the motion of the electrons in the M_{33} orbits rises to its maximum value in Fe(26) and that this field is only compensated by the contrary one produced by the 4 electrons moving in the M_{32} orbits in Cu(29). Thus in general the magnetic energy of the excited atom is due to the magnetic interaction of the radiating electron with the different shells in the atom. The contributions made by each of them is at present difficult to calculate. If the rather low value of $\Delta\nu_{mag}/R(Z-3.5)^3$ for

[7] For references see (6).

Zn(30) which was noticed previously is not due to experimental error, then it may probably be attributed to the fact that in Zn the N_{11} shell is completed.

Similar periodic variation in the separation $\Delta\lambda$ for the $L\alpha$ doublets of the elements Nb(41) to Ur(92) has been tabulated by Ray,[8] and may also be attributed to magnetic origin. The first of these periods is due to the second transition group of elements from Nb(41) to Pd(46), in which the N_{32} and N_{33} sub-levels are completed. The separations $\Delta\lambda$ for all the elements of this group are not contained in Ray's paper, and the order of accuracy in the measurement is not so great as that for the $K\alpha$ doublets. The maximum separation obtained is due to the $L\alpha$ doublet of Mo(42) the next being that of Ru(44). If these measurements are correct then it would indicate that the N_{32} sub-level is completed first and then the N_{33}, contrary to the order in which the M_{32} and M_{33} sub-levels are formed.

In conclusion I wish to express my thanks to Messrs. H. P. De and R. Mukherjee for helping me with the calculations contained in this paper.

UNIVERSITY COLLEGE OF SCIENCE,
DEPARTMENT OF PHYSICS,
CALCUTTA, INDIA,
December 22, 1925.

[8] Ray, Phil. Mag. **48**, 707 (1924).

THE K EMISSION SPECTRA FOR ELEMENTS TIN (50) TO HAFNIUM (72)

By J. M. Cork and B. R. Stephenson

Abstract

Using an x-ray tube and transmission spectrograph as previously described, measurements were made of the K series emission wave-lengths of elements from Sn (50) to Hf (72), except Xe (54) and Ho (67). The β line is resolved for most of the elements into two components β' and β, having a wave-length difference of about .76 x-units. The wave-length difference between the α' and α lines varies from about 4.4 x-units for tin to 4.84 x-units for hafnium. This doublet difference when plotted with atomic number gives a curve with slight irregularities for groups of points, which may bear a relation to the method of adding additional electrons in the process of atom building.

THE K series emission wave-lengths for the elements Sn (50), Sb(51) and Te(52) have been measured by Leide.[1] For the elements Ba(56) to Nd(60) and Sa(62), Gd(64), Dy(66) and Er(68), measurements were reported by one of us.[2] In these measurements it was later found that an error existed due to an inaccuracy in the scale of the expansion micrometer gauge used to measure the distance between the slit and photographic plate in the x-ray spectrograph. When proper correction is made the previously published values are found to have a slight consistent error. More plates have, however, been taken for all these elements on the larger spectrograph used in this investigation. Liede[3] has recently published wave-length values for many of the K series lines of some additional elements.

If measurements for successive elements are to be compared, it is desirable that they be made with the same spectrograph. In the present paper the K emission spectra of all elements from Sn(50) to Hf(72) with the exception of Ho(67) and Xe(54) have been investigated.

Apparatus

X-ray tube. The x-ray tube was similar in construction to that previously described[4], having ground joints at both anode and cathode ends. The compounds containing the elements under investigation were placed on the face of the water cooled target by first applying to

[1] See Siegbahn, Spectroscopy of X-Rays, 1925.

[2] Cork, Phys. Rev. **25**, 197 (1925).

[3] Leide, Dissertation, Lund, (1925).

[4] Stephenson and Cork, Phys. Rev. **27**, 138 (1926).

the target face a thin coating of shellac and then covering it with a thin coating of the powder. The whole end of the target was then heated to expel the volatile matter. One application of material in this way was generally sufficient for the necessary exposures.

X-ray spectrograph. The x-ray spectrograph used in this investigation has been previously described.[4] The large distance (75.593 cms) between the slit and the photographic plate resulted in a very good resolution of the K series lines, so that the β line which normally appears as a broad single line showed as a doublet. A calcite crystal was used. The grating space assumed in the computations, since the

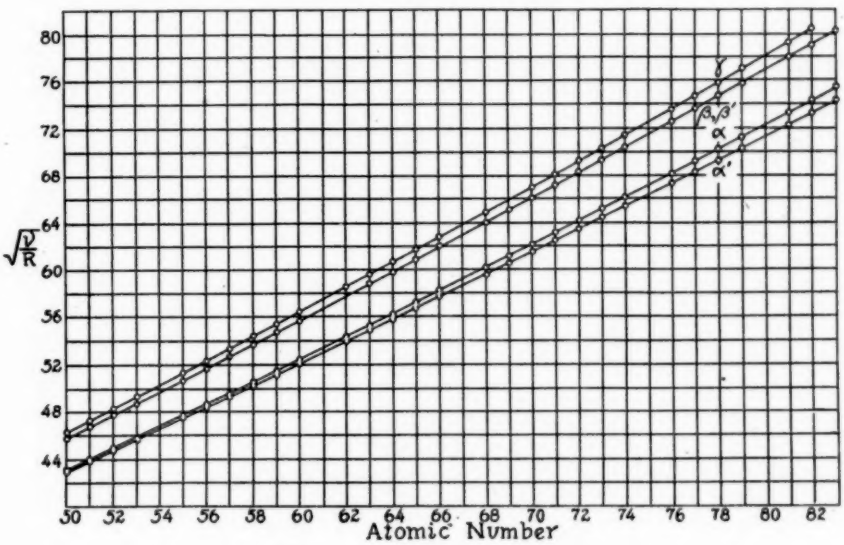

Fig. 1. Values of $\sqrt{\nu/R}$ for K series lines plotted against atomic number.

basement room in which the experimental work was performed was uniformly constant at about 22°C, was the value given by Siegbahn and Compton at 22°C, 3.02916A. No correction is made for the refraction of x-rays by the crystal material.

Results

Table I presents a complete summary of the data obtained. Along with the wave-length values are given the frequency numbers ν/R and the square root of ν/R where ν is the reciprocal of the wave-length in cms and R is the Rydberg number 109,737. Fig. 1 shows the square root of ν/R plotted with atomic number. In Table II are recorded values for the two components of the β line (β' and β) for all of the elements

except the first three. Most of the rare earth compounds used were not chemically pure but contained neighboring elements as impurities so that overlapping spectra were obtained. In only one case, however, did lines occur so close together as to make the measurement of one of

TABLE IA

Summary of data for K series emission lines, Kα and Kα′

Element	α′ λ	α′ ν/R	α′ $\sqrt{\nu/R}$	α λ	α ν/R	α $\sqrt{\nu/R}$
50Sn	494.06	1844.4	42.947	489.66	1861.1	41.139
51Sb	474.00	1922.5	43.846	469.54	1940.8	44.054
52Te	455.04	2002.6	44.746	450.51	2022.8	44.975
53I	436.94	2085.5	45.668	432.43	2107.3	45.905
55Cs	403.98	2255.7	47.485	399.48	2281.1	47.761
56Ba	388.91	2343.1	48.404	384.31	2371.1	48.692
57La	374.60	2432.6	49.321	369.96	2463.1	49.630
58Ce	360.97	2524.5	50.242	356.37	2557.1	50.567
59Pr	348.05	2618.2	51.169	343.40	2653.6	51.513
60Nd	335.96	2712.4	52.081	331.31	2750.5	52.445
62Sa	313.20	2909.5	53.940	308.54	2953.4	54.346
63Eu	302.69	3010.5	54.868	297.99	3058.1	55.300
64Gd	292.41	3116.4	55.825	287.73	3166.9	56.275
65Tb	282.94	3220.7	56.751	278.19	3275.7	57.234
66Dy	273.64	3330.1	57.707	268.87	3389.2	58.217
68Er	256.72	3549.6	59.578	251.99	3616.2	60.135
69Tm	248.61	3665.4	60.543	243.87	3736.7	61.129
70Yb	240.99	3781.3	61.493	236.22	3857.7	62.111
71Lu	233.58	3901.3	62.461	228.82	3982.4	63.107
72Hf	226.53	4022.7	63.424	221.73	4109.8	64.108

TABLE IB

Summary of data for K series emission lines, Kβ, β′, and Kγ

Element	β′, β (ave) λ	β′, β (ave) ν/R	β′, β (ave) $\sqrt{\nu/R}$	γ λ	γ ν/R	γ $\sqrt{\nu/R}$
50Sn	434.68	2096.4	45.786	425.13	2143.5	46.298
51Sb	416.42	2188.4	46.780	407.20	2237.9	47.306
52Te	399.29	2282.2	47.772	390.49	2333.6	48.308
53I	383.54	2376.0	48.745	374.61	2432.5	49.320
55Cs	353.99	2574.2	50.737	345.16	2640.5	51.386
56Ba	340.56	2675.8	51.726	332.22	2742.9	52.370
57La	327.68	2781.0	52.735	319.66	2850.7	53.392
58Ce	315.37	2889.5	53.756	307.70	2961.5	54.419
59Pr	304.00	2997.6	54.751	296.25	3076.0	55.462
60Nd	293.13	3108.7	55.756	285.73	3189.3	56.474
62Sa	272.88	3339.5	57.788	265.75	3427.5	58.545
63Eu	263.47	3458.8	58.811	256.45	3553.4	59.611
64Gd	254.33	3581.0	59.859	247.62	3680.1	60.664
65Tb	245.90	3705.8	60.875	239.12	3810.9	61.733
66Dy	237.49	3837.1	61.945	231.28	3940.1	62.770
68Er	222.58	4094.2	63.986	216.71	4205.1	64.847
69Tm	215.23	4234.0	65.069			
70Yb	208.75	4365.4	66.071	203.22	4484.1	66.963
71Lu	202.12	4508.7	67.146	196.49	4637.7	68.100
72Hf	195.49	4661.4	68.275	190.42	4785.5	69.178

them impossible. The γ line for Tm(69) was overlapped by the β line for Yb(70) which was found as an impurity in many of the compounds.

TABLE II

Values for K series β' and β lines.

Element	β'			β		
	λ	ν/R	$\sqrt{\nu/R}$	λ	ν/R	$\sqrt{\nu/R}$
53I	383.92	2373.6	48.720	383.15	2378.4	48.769
55Cs	354.36	2571.5	50.710	353.62	2576.9	50.763
56Ba	340.89	2673.2	51.700	340.22	2678.5	51.752
57La	328.09	2777.4	52.701	327.26	2784.5	52.769
58Ce	315.72	2886.2	53.725	315.01	2892.8	53.787
59Pr	304.39	2993.7	54.715	303.60	3001.5	54.786
60Nd	293.51	3104.7	55.720	292.75	3112.7	55.791
62Sa	273.25	3334.9	57.749	272.50	3344.1	57.828
63Eu	263.86	3453.6	58.767	263.07	3463.9	58.855
64Gd	254.71	3577.7	59.814	253.94	3584.4	59.904
65Tb	246.29	3699.9	60.827	245.51	3711.7	60.924
66Dy	237.87	3830.9	61.895	237.10	3843.3	61.995
68Er	223.00	4086.4	63.925	222.15	4102.0	64.047
69Tm	215.58	4227.0	65.015	214.87	4241.0	65.123
70Yb	209.16	4356.8	66.006	208.34	4373.9	66.136
71Lu	202.52	4499.6	67.079	201.71	4517.7	67.214
72Hf	195.83	4653.3	68.216	195.15	4669.5	68.334

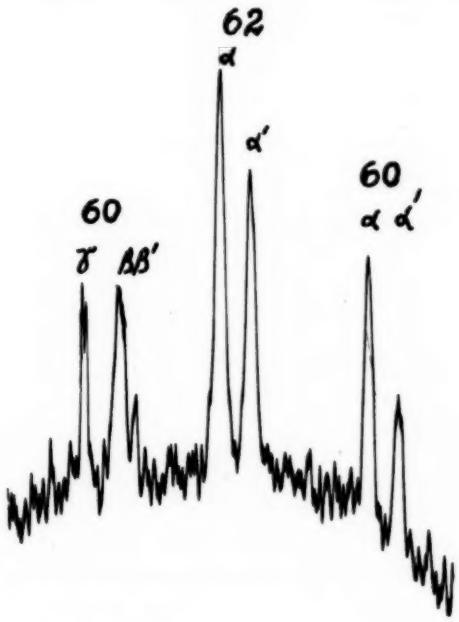

Fig. 2. Micro-photogram of K series lines of Sa(62) and Nd(60).

Fig. 2 shows a typical micro-photogram of a portion of one of the plates, which shows the presence of the elements Sa(62) and Nd(60).

Although the curve of the micro-photogram gives some notion of the relative intensity of the lines, it cannot be taken as an absolute measure because several factors, such as inequality in exposure for the different wave-lengths, non-linear density-exposure relation for the photographic film, etc., render the ordinates inaccurate as measures of intensity.

The lines were photographed on each side of the zero position and the distance between the same spectral line on opposite sides was measured. In this spectrograph a distance between lines of 10 cms

TABLE III

Some wave-length differences between K series lines.

Element	$\lambda_{\alpha'}-\lambda_{\alpha}$	$\lambda_{\beta}-\lambda_{\gamma}$	$\lambda_{\beta'}-\lambda_{\beta}$
50Sn	4.40	9.55	——
51Sb	4.46	9.22	——
52Te	4.53	8.80	——
53I	4.51	8.93	0.77
55Cs	4.50	8.83	0.74
56Ba	4.60	8.34	0.67
57La	4.64	8.02	0.83
58Ce	4.60	7.67	0.71
59Pr	4.65	7.75	0.79
60Nd	4.65	7.40	0.75
62Sa	4.64	7.13	0.75
63Eu	4.70	7.02	0.79
64Gd	4.68	6.71	0.77
65Tb	4.75	6.78	0.78
66Dy	4.77	6.21	0.77
68Er	4.73	5.87	0.85
69Tm	4.74	——	0.71
70Yb	4.77	5.53	0.82
71Lu	4.76	5.63	0.81
72Hf	4.80	5.07	0.68
73Ta	4.85	5.39	——
74W	4.83	5.24	——
76Os	4.86	4.86	——
77Ir	4.85	4.74	——
78Pt	4.81	4.83	——
79Au	4.87	4.76	——
81Tl	4.86	4.72	——
82Pb	4.88	4.81	——
83Bi	4.84	——	——

corresponded to a wave-length of about 400 x-units. The α and α' lines were very sharp and well defined and their distance apart readily measurable to .01 mm involving a probable error of $\pm .04$ x-units. While the β line is normally very broad the components when resolved are more clearly defined. The γ line is somewhat diffuse and rather weak in intensity unless the α lines are over exposed, hence the error for the β and γ lines may be considerably greater than for the α lines.

Column 3 of Table III shows the results obtained by subtracting the wave-length of the α line from that of the α' line for each of the elements. This wave-length difference is associated with the energy difference between the L_2 and L_3 electron levels. The same results are shown graphically in Fig. 3. It may be observed that there is in general an increase in $\Delta\lambda$ with atomic number from about 4.40 x-units for tin to 4.80 for hafnium. In the region of the rare earth elements, however, certain groups of points seem to show a systematic deviation from a smooth curve by amounts slightly greater than the probable experimental error. These changes in slope may have significance in the way electrons are added in the process of atom building. An increase in slope might be interpreted as an indication that the electron is added in such a way that its screening effect is greater by an unusual

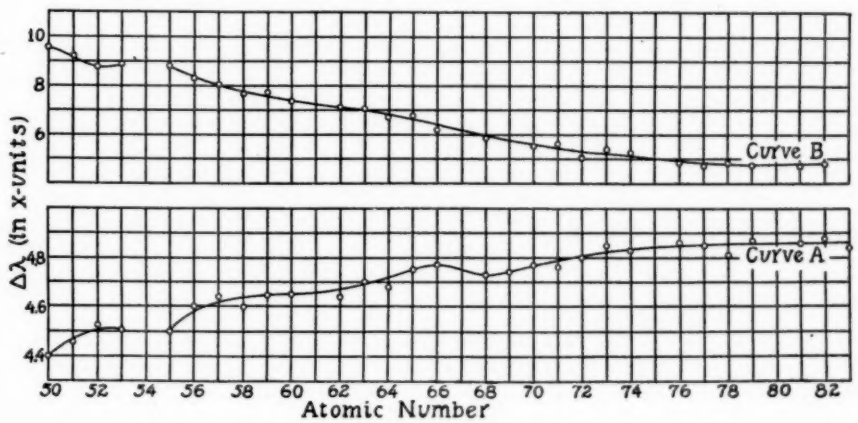

Fig. 3. Wave-length differences, $(\alpha'-\alpha)$ and $(\beta-\gamma)$ plotted against atomic number.

amount upon the L_3 level than upon the L_2 level. This might be the case if the electron is added in the very eccentric orbits such as the 4_1, 5_1, 6_1, or perhaps 4_2, 5_2, 6_2 levels since in these the electron penetrates close to the nucleus during a portion of its path. Thus an upward slope might be expected for the elements 55 and 56 since for these elements the last electrons are added in a 6_1 orbit. However, for 57 et seq. it is presumed electrons are added in such a way as to fill up the vacancies in the four quantum or five quantum orbits. According to the plan of Stoner these unfilled orbits are not the most eccentric while in the Bohr and Coster arrangement two electrons must be added to each of the eccentric 4_1, 4_2, 5_1, and 5_2 orbits. Too much confidence must not be placed herein because the deviations are of the

same order of magnitude as the experimental error. Siegbahn and Ray[5] have observed the variation in this doublet difference for lighter elements showing very noticeable irregularities. In the region of the alkali metals K and Ca the curve had a negative rather than positive slope while for Rb and Sr the slope was positive. The L $\alpha\alpha'$ doublet has also been investigated by Ray[6] for the elements mentioned in this paper and periodic deviations from a smooth curve observed.

TABLE IV

Element	λ_γ	λK_{abs}*	$\lambda_\gamma - \lambda K_{abs}$*	$\Delta\nu/R$ ($L_\beta - L_a'$)	$\Delta\nu/R$ ($K_a - K_a'$)
50Sn	425.13	423.94	1.19	16.72	16.7
51Sb	407.20	406.09	1.11	18.30	18.3
52Te	390.49	389.26	1.23	20.00	20.2
53I	374.61	373.44	1.17	21.70	21.8
55Cs	345.16	344.07	1.09	25.59	25.4
56Ba	332.22	330.70	1.52	27.74	28.0
57La	319.66	318.14	1.52	30.01	30.5
58Ce	307.70	306.26	1.44	32.05	32.6
59Pr	296.25	295.1	1.15	35.02	35.4
60Nd	285.73	284.58	1.15	37.86	38.1
62Sa	265.75	264.4	1.3	43.95	43.9
63Eu	256.45	254.8	1.6	47.17	47.6
64Gd	247.62	246.2	1.4	50.64	50.5
65Tb	239.12	237.6	1.5	54.36	55.0
66Dy	231.28	230.1	1.2	58.24	59.1
68Er	216.71			66.81	66.6
69Tm				71.27	71.3
70Yb	203.22	201.6	1.6	76.08	76.4
71Lu	196.49	195.1	1.4	81.11	81.1
72Hf	190.42			86.76	87.1

* Siegbahn, English Edition, 1925.

Column 4 of Table III shows in a similar way the result obtained by forming the wave-length difference between the average β and γ lines for each element. This wave-length difference decreases in general with atomic number from 9.55 x-units for tin to 5.07 for hafnium. These results are also shown graphically in Fig. 3, curve *B*. This wave-length difference is associated with the energy difference between the $M_{2,3}$ and $N_{2,3}$ orbits. It may be observed that here also certain groups of points deviate somewhat from a smooth curve. This is observable particularly well in the region of elements 53 to 57.

Column 5 of Table III shows the wave-length differences for the β' and β lines. This wave-length difference is apparently constant, except for experimental error, and has an average value of .76 x-units.

[5] Siegbahn and Ray, Arkiv. för Matematik, Astronomie och Fysik, **18, 19**; also Siegbahn, Spectroscopy of X-Rays, 1925.

[6] Ray, Phil. Mag. **48**, 707 (1924).

Table IV, column 5, shows a summary of the wave-length difference between the γ line and the K absorption edge for each element. The square root of the frequency difference between the K absorption edge and the γ line should, when plotted with atomic number, give a line of positive slope with abrupt changes in slope in the region of the rare earth elements as predicted by Bohr and Coster. As these absorption measurements have been made by different observers and some are undoubtedly in error this curve is not presented. In columns 6 and 7 the frequency difference for the Kα doublet is compared with that for the Lβ and Lα' lines. The agreement is in most cases fairly close.

UNIVERSITY OF MICHIGAN,
December 5, 1925.*

* Received February 18, 1926.—Ed.

THE L ABSORPTION LIMITS OF TUNGSTEN: PHOTOMETRIC MEASUREMENTS

By C. B. Crofutt

Abstract

In a previous paper both the absorption and emission spectra of tungsten were photographed simultaneously on the same plate. It has since seemed advisable to make a photometric analysis of the original plates showing the L absorption bands. The results give for L_1, 1.2117A, and for L_2, 1.0708A, as compared with the former eye measurements of 1.2122A and 1.0716A, though the last are regarded by the author as more reliable. The mean variation in the measurements is less than .0002A. L_1 is clearly between β_8 and β_{10} and L_2 between γ_6 and γ_3, indeed between γ_6 and a new line, 1.0699A.

IN A previous work[1] both the absorption and emission spectra of tungsten were photographed simultaneously on the same plate. Because accuracy in the measurement of the absorption limits is important, it seemed advisable to measure them on the original plates by means of photometric curves.

The photomicrograph[2] used was built and used at the University of Iowa. A complete description will be published later. Briefly it consists of a suitable lens system whereby a narrow beam of light (from .06 mm. to .12 mm) can be passed through the photographic plate and allowed to fall upon one junction of a thermocouple connected to a sensitive galvanometer, the deflection of which is a measure of the transparency of the plate.

It soon developed that, while the plates appeared very good to the eye and under low magnification, they were not of sufficient quality to give photometric curves in which the order of magnitude of the irregularities was less than the variations to be measured. These local irregularities were not entirely due to the individual grains of silver in the emulsion but to a great extent to the lack of uniformity of the emulsion. There were spots on the plate of the order of magnitude of a square millimeter which would differ in density from a neighboring one by fifty percent. Unfortunately the thermocouple junction had a length of sensitive spot of the order of only a millimeter.

Because of the irregularities in a plate, a single photometric curve could not be used to locate the absorption bands with certainty. This

[1] C. B. Crofutt, Phys. Rev. 24, 9 (1924).

[2] The microphotometer is a modification of that described by Harrison, J.O.S.A. & R.S.I., 10, 157 (1925). In this article are references to the literature.

made necessary several curves over the same region with the setting displaced parallel to the spectrum lines. These curves were then averaged graphically. The resulting curves, called average curves, are the ones shown. No curve here presented and showing an absorption band is the average of less than two.

The results are shown in Figs. 1, 2 and 3. Fig. 1 shows the region in the neighborhood of the L_1 absorption band. Curves *a*, *b* and *c* are the average of two or three parallel curves obtained from three separate exposures. Curve *d* is the average of the three curves *a*, *b* and *c*.

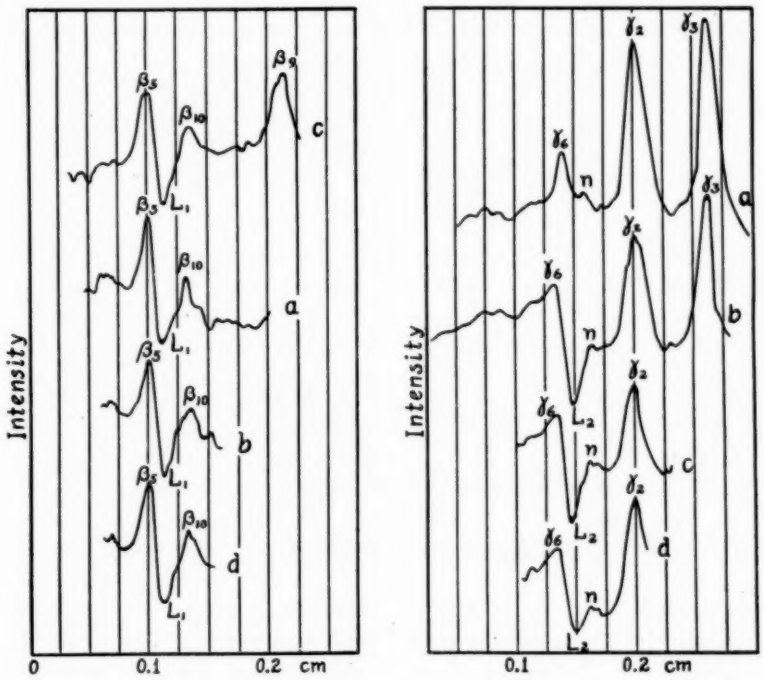

Fig. 1. Average photometer curves showing L_1 absorption.
Fig. 2. Average photometer curves: (a) emission, (b), (c), (d) emission and L_1 absorption.

Fig. 2 shows the region in the neighborhood of the L_2 absorption band. Curve *a* shows the emission spectrum without the absorption band. It will be seen that the line marked *n* is one of the new lines reported in the previous paper. Curves *b* and *c* were taken under identical conditions except that the widths of the beams of light passing through the plate were 0.1 mm and .06 mm, respectively. Curve *d* is the average of four curves taken from two plates.

Fig. 3, the average of three parallel curves, shows the region in the neighborhood of the L_3 absorption band. It is the least satisfactory of the three.

All curves in Figs. 1 and 2 have been translated so that corresponding points on the curves have the same abscissas. The peaks of β_5 and γ_2 have been taken as corresponding points for this purpose.

It is seen that the absorption L_1 falls between the emission lines β_5 and β_{10} and that L_2 falls between the emission lines γ_6 and γ_2. Since the wave-lengths of β_5, β_{10}, γ_6 and γ_2 as previously reported have not been questioned, these curves show conclusively that L_1 falls between the wave-lengths 1.2133A and 1.2099A and that L_2 falls between wave-lengths 1.0723A and 1.0659A. These wave-lengths are those measured assuming the grating space of rock salt to be 2.8140A.

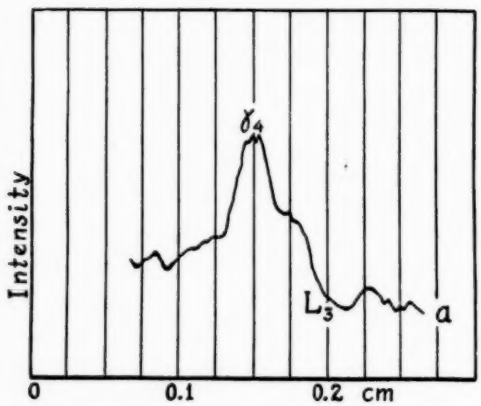

Fig. 3. Average photometer curve showing L_3 absorption.

It is noticed that all the curves show on the short wave side of the absorption limit a decrease of radiation below that of the continuous spectrum in the absence of the absorber. These are the "white lines" referred to in the literature and apparently found only with photography.

TABLE I

Interpolated values of wave-lengths of L_1 and L_2 absorption bands

	L_1	L_2			
	Fig. 1(d)	Fig. 2(b)	Fig. 2(c)	Fig. 2(d)	Ave.
Long wave-length edge:	1.2116	1.0709	1.0709	1.0708	1.0709
Peak:	1.2120	1.0708	1.0710	1.0708	1.0709
Short wave-length edge:	1.2116	1.0704	1.0707	1.0706	1.0706
Average:	1.2117				1.0708

In the judgment of the author the photometer curves do not furnish as accurate a measurement of the wave-lengths as those already published which were obtained by direct measurement of the plates, using a dividing engine and a low powered microscope. However, on account of the importance of accurate measurements it seemed advisable to determine the wave-lengths corresponding to absorptions L_1 and L_2 from the curves. This was done by interpolation, using β_5 and β_{10} as reference lines for L_1 and γ_6 and γ_2 as reference lines for L_2 with the wave-lengths of the four as given in the preceding paragraph. The measurements for these interpolations were taken from three different

TABLE II

Comparison of results

	L_1	L_2
Duane	1.2140	1.0730
Direct Measure	1.2122	1.0716
Photometric Meas.	1.2117	1.0708

points on the lines and bands: the long wave-length edges, the peaks, and the short wave-length edges. The results are shown in Table I. These results are compared with previous results in Table II. It is seen that the wave-lengths obtained from the photometric measurements of the plates are somewhat shorter than the previous results.

In conclusion, photometric curves have been obtained showing the L_1, the L_2, and the L_3 absorptions of tungsten. The results are in agreement with the results previously reported, which are regarded by the author as the more reliable.

I wish to acknowledge indebtedness to the members of the staff of the physical laboratory at the University of Iowa and especially to Professor Stewart, for their interest in the work.

UNIVERSITY OF ARKANSAS,
January 25, 1926.

NATURAL IONIZATION IN GASES

By James W. Broxon

Abstract

Measurements of the *pressure variation* of the natural ionization in air, nitrogen, oxygen and carbon dioxide contained in a steel sphere of one foot inside diameter, made by H. F. Fruth for pressures from 1 to 75 atmospheres, were repeated with slight modifications. Results obtained corresponded with those of Fruth with the following exceptions: (1) although the pressure rate of variation of the natural ionization at high pressures was very small (0.4 to 1.0 ion/cc sec. atm.) no abrupt change in the rate of variation and no true "saturation" value of the ionization were observed; (2) no "anomalous" behavior was noted in the case of commercial nitrogen. Measurements to detect the *variation with size of chamber* were carried out with spherical iron ionization chambers of 7, 9, and 12 in. respective internal diameters. The rate of production of ions per cc at high pressures did not vary unidirectionally with the size of the ionization chambers, but was least in the 9 in. sphere. To study the *effect of the lining* the experiments were repeated with oxygen in each of the spheres lined with aluminum of 1/16 in. thickness, and in the 12 in. sphere lined with copper of 1/16 in. thickness. The aluminum lining increased the ionization at low pressures, and decreased its pressure rate of variation at high pressures. The copper lining reduced the absolute value of the ionization at high pressures. The *effect of water vapor* on the natural ionization in aged, dust-free air, or upon its variation with pressure was found to be negligible. Both the absolute and the fractional *variation of the natural ionization with time* were found to depend upon the pressure, the average value of the former during a 24 hr. period being about twice and that of the latter being about 1/5 as great in oxygen at 55.4 atm. pressure as in air at atmospheric pressure. Very slight evidence of a singly periodic diurnal variation in air at atmospheric pressure was observed. Attempts to determine the *effects of slow chemical reactions* upon the natural ionization in air and oxygen at atmospheric pressure led to negative results.

Introduction

THIS paper has to do with the ionization occurring in closed vessels apart from the action of definitely recognized and localized ionizing agents, a problem first attacked from the present point of view by C. T. R. Wilson[1] and Elster and Geitel.[2] In their work on the variation of the natural ionization with pressure, it was found by Downey[3] in the case of air, and by Fruth[4] in the cases of "purified" air and oxygen,

[1] C. T. R. Wilson, Proc. Camb. Phil. Soc. **11**, 32 (1900); Roy. Soc. Proc. **A68**, 151 (1901).

[2] H. Geitel, Phys. Zeits. **2**, 116 (1900);
J. E. Elster and H. Geitel, Phys. Zeits. **2**, 560 (1901).

[3] K. M. Downey, Phys. Rev. **20**, 186 (1922).

[4] H. F. Fruth, Phys. Rev. **22**, 109 (1923).

that the natural ionization in a gas in a spherical steel container increased with the pressure until pressures of about 46 and 52 atmospheres, respectively, were attained, and remained constant as the pressures were still further increased. Fruth found a similar saturation value in the case of carbon dioxide at 61 atmospheres. His results show no such saturation value in the case of nitrogen either as prepared commercially or in the laboratory. Moreover, no saturation value was observed in the case of oxygen and nitrogen which had been mixed in approximately the same ratio as they occur in air.

It was with the particular object of further investigating the occurrence of these saturation values and of discovering the reason for the

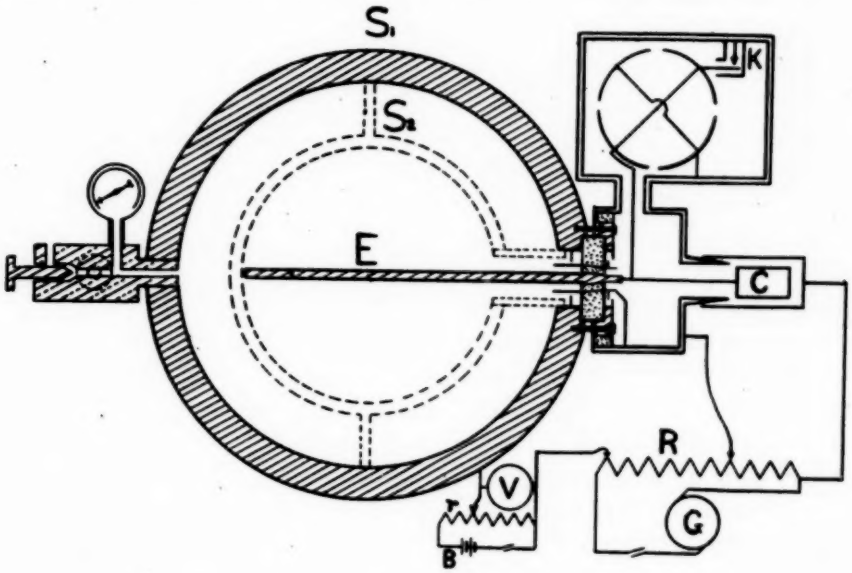

FIG. 1. Diagram of apparatus.

"anomalous" behavior of nitrogen, that the present work was undertaken at the suggestion of Professor W. F. G. Swann.

APPARATUS AND MANIPULATION

The ionization chamber consisted of the same iron sphere of one foot internal diameter, with walls of one inch thickness, which was used by Fruth, and the experimental arrangement corresponded closely with that described by him, certain modifications being made as shown in Fig. 1. The guard system was slightly modified, lead was substituted for the red rubber gasket, and the compensating condenser, C, was fixed. Observations and calculations were also made in essen-

tially the same manner as in Fruth's work, all the precautions listed by him being taken in this instance.

In addition to the original sphere of 12 in. internal diameter, two iron spheres were cast, their thickness being 1/4 in. and their diameters 7 in. and 9 in., respectively. These could be inserted individually within the 12 in. sphere and held concentric with it by means of collars and a connecting pipe, as shown by the dotted S_2 in Fig. 1, E being made correspondingly shorter. As in the case of S_1, these spheres were actually cast as hemispheres and bolted together, but no attempt was made to make the inner spheres gas-tight, the pressure inside them being everywhere the same as that inside S_1.

In the present case, electrometer fibers from 2 to 5 times as sensitive as those used by Fruth were employed; three individual sets of readings were taken in practically every instance at each pressure; and the gases were passed first through the drying tube and then through the dust remover. The calibration constant, K, for a given arrangement of the ionization chamber, was usually considered at all pressures[5] to have the same value as at atmospheric pressure. In the case of carbon dioxide, however, a considerable variation was observed, and K was determined at each pressure. Saturation currents were assured by using ionization chamber potentials such that an increase of less than 0.3 percent in the currents resulted when the potentials were doubled.

No elaborate system of shielding was adopted. The thick walls of the ionization chambers themselves provided a certain amount of shielding from external radiations. In one instance, with the 9 in. sphere in position and filled with oxygen at a pressure of 200 lbs. per sq. in., measurements of the natural ionization were made before and after the placing of boxes of lead storage battery plates in the vicinity of the ionization chamber. These plates provided roughly a 6 in. lead wall subtending a solid angle of approximately $4\pi/3$ at the center of the chamber. With due consideration for its variation with time, the natural ionization could not be considered to have been decreased by more than $3\frac{1}{2}$ percent by the lead shield. An actual decrease, however, appears to have occurred.

The hydrogen and hydrogen sulphide used were formed in Kipp generators by the action of hydrochloric acid upon zinc and upon ferrous sulphide, respectively. The other gases used were purchased from commercial producing companies, with the exception of air which was compressed in the laboratory.

[5] It should be noted at this point that throughout this paper all pressures referred to in terms of lbs per sq. in. are pressures *in excess* of atmospheric pressure.

Results and Discussion

Pressure Variation. In order to determine the variation with pressure of the natural ionization in certain gases, the natural ionization occurring in air, oxygen, nitrogen and carbon dioxide was measured with the 12 in. sphere as ionization chamber, at various pressure intervals between atmospheric pressure and pressures in the neighborhood of 1000 lbs. per sq. in. The results are shown in Figs. 2, 3 and 5.

In view of the announced purpose of this research, perhaps the most noticeable feature of the results obtained is the fact that in no instance was a true saturation value observed. According to Fruth's[4] results a saturation value of the ionization should have been obtained at 53 atmospheres or about 779 lbs. per sq. in., in the cases of oxygen and of air contained in the 12 in. sphere. However, although the above pressure was exceeded by from 13.6 to 22.5 atmospheres with both oxygen and air in all the cases in which the pressure variation with these two gases was investigated, the curves in no instance became horizontal nor was there evidence of a sharp break at any point. On the other hand, all the curves obtained are smooth and are everywhere concave downward, i.e., toward the pressure-axis. It is seen, therefore, that with both air and oxygen the slopes of the P-n curves decreased gradually with pressure, so that the curves may be considered to be approaching saturation values. However, the pressure rates of change of slope at the highest pressures are very small and it is only possible to conjecture as to whether the curves would finally reach saturation values, whether their slopes would continually decrease without vanishing, or whether the curves would become straight lines with constant small slopes. The gradual decrease in the curvature of these curves together with the form of the curves for nitrogen and carbon dioxide, tend rather to persuade one toward the latter view. The pressure curves obtained with nitrogen and carbon dioxide are practically straight lines at pressures above 800 and 500 lbs. per sq. in., respectively.

In their most important aspects, the results described in this paper agree with those of Downey and Fruth. In each case investigated, with whatever gas, size of ionization chamber or nature of lining, at the highest pressures obtained the rate of increase in the natural ionization with pressure was very small, being in no case greater than one ion (of one sign) per cc per sec. per atm. The values given in Table I for the least slopes agree very well with the values of Δq given in Table II of Dr. Downey's 1922 paper for the CD portion of her curves, as well as with the final slopes of Fruth's curves apart from the

horizontal portions of his curves for air and oxygen. As nearly as can be determined, if we neglect these portions of Fruth's curves, we have as the ratios of the final slopes of his curves to the final slopes of the curves in this paper for the same gases in the unlined 12 in. sphere: 1.67 for air; 1.37 for oxygen; 1.52 for nitrogen; 1.67 for carbon dioxide. If his "saturation" values be neglected, then, it would appear that the final slopes of his curves are from 1 1/3 to 1 2/3 times as large as those of curves obtained similarly in this investigation. In other words, there is very close agreement.

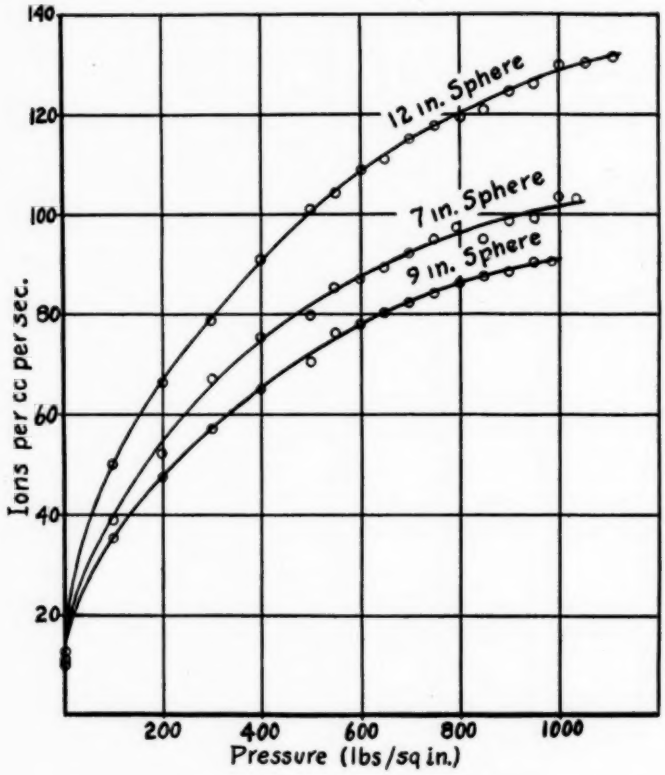

FIG. 2. Variation with pressure of the natural ionization in air.

It may be noted that some of the curves obtained by the writer are of the same general type as obtained by Wilson[6] for pressures up to 40 atmospheres. Evidence recently provided by Millikan[7] for the existence of a very penetrating cosmic radiation points toward the

[6] W. Wilson, Phil. Mag. 17, 216 (1909).

[7] R. A. Millikan, Science 62, 445 (1925); Nature 116, 823 (1925); Proc. Nat. Acad. Sci. 12, 48 (1926) especially p. 51.

probability that ionization due to this source at sea level should be very small, and of about the order herein obtained per atmosphere increase of pressure at the highest pressures. Swann[8] has drawn attention to the smallness of the effect to be expected from this source.

Variation with Size of Ionization Chamber

The magnitude of the natural ionization occurring in a gas at high pressures and also its rate of variation with pressure, were found to depend upon the size of the ionization chamber. This dependence is

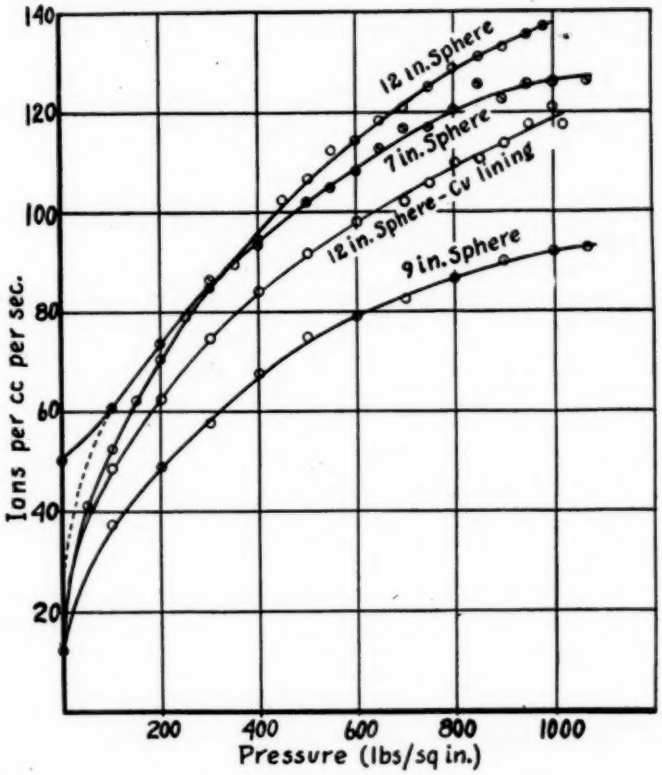

FIG. 3. Variation with pressure of the natural ionization in oxygen.

readily seen upon inspection of Figs. 2, 3 and 4. One outstanding fact which was not expected is that at the higher pressures the curves for the 7 in. sphere lie between those for the 12 in. and 9 in. spheres. Thus the ionization (ions/cc sec.) must pass through a minimum as the size of the chamber is varied. This peculiarity exists at all pressures above 1 atm. excepting in the case of oxygen in the unlined spheres, in which

[8] W. F. G. Swann, Nat. Res. Coun. Bull. 17, 3, 65 (1922).

case the curve for the 7 in. sphere crosses that for the 12 in. sphere and the former has an abnormally high value at atmospheric pressure. If the ionization were chiefly due to soft radiations from the walls of the ionization chamber and if the magnitude of these radiations could be considered to be proportional to the area as long as the walls were made of the same material, then an increase in the number of ions per cc per sec. should be expected to accompany a decrease in the

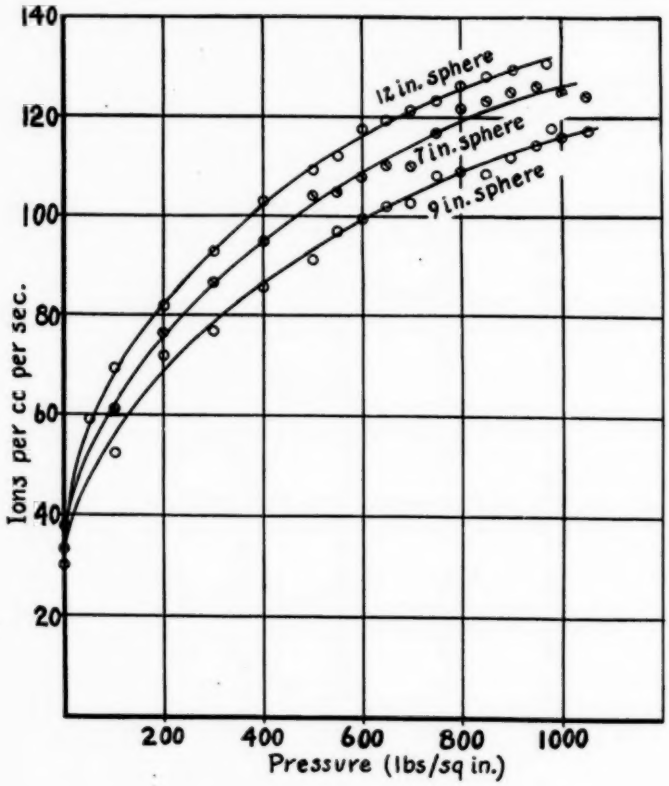

FIG. 4. Variation with pressure of the natural ionization in oxygen. Spheres lined with aluminum.

volume with its accompanying increase in the ratio of area to volume. A theoretical discussion of these matters will appear in a subsequent publication.

At atmospheric pressure, the rate of production of ions per cc in the 12 in. sphere was in each case slightly less than the corresponding ionization in the smaller spheres. However, without more extended series of readings with the various spheres at atmospheric pressure, this observation should not be considered to be well established.

One interesting observation is (see Table I) that the smallest slope or the least change in the number of ions per cc per sec. per atmosphere increase of pressure, apparently decreased slightly with the size of the spherical ionization chamber. The smallest value observed was about 0.18 ion/cc sec. atm. in oxygen contained in the 7 in. sphere at a pressure of 1070 lbs. per sq. in.

Dependence upon Kind of Gas

As has been mentioned previously, the curvature in the nitrogen and carbon dioxide curves appears to be quite definitely zero over considerable distances at their high-pressure ends. Although all the values at atmospheric pressure were of about the same magnitude, the values of the ionization in nitrogen and carbon dioxide at the higher pressures were considerably greater than the values at corresponding pressures in the other gases in the same 12 in. sphere.

It is seen upon reference to Table I that the least slopes of the oxygen and air curves are of about the same magnitude, whereas those for nitrogen and carbon dioxide are considerably greater and about equal. In fact, upon superposition of the nitrogen and carbon dioxide curves (Fig. 5), it is seen that they nearly coincide throughout, the latter being a little more concave at the lower pressures, while in the former the concavity is smaller but more persistent.

Table I

Least slopes of pressure-ionization curves.

Gas	Ionization Chamber	Lining	$\left(\frac{\text{Least slope}}{\frac{\text{ions}}{\text{cc sec. atm.}}}\right)$.
Air	12-in.	None	0.40
Air	9-in.	None	0.32
Air	7-in.	None	0.26
O_2	12-in.	None	0.65
O_2	9-in.	None	0.24
O_2	7-in.	None	0.18
O_2	12-in.	Al	0.50
O_2	9-in.	Al	0.41
O_2	7-in.	Al	0.40
O_2	12-in.	Cu	0.65
N_2	12-in.	None	0.97
CO_2	12-in.	None	1.00
Air+H_2O Vapor	12-in.	None	0.90

The curve for moist air shown in Fig. 5 was obtained by pouring 20 cc of distilled water into the 12 in. sphere, unlined, after which aged, dry, dust-free air was admitted to a pressure of 750 lbs per sq. in. Examination of the curve shows that there was no particular difference

(so far as observations extended) between the ionization occurring in this case and that in dry air in the same chamber. Values at the higher pressures were slightly smaller in the former case than in the latter, but the divergence between the two curves is small and gradual. The final least slope of the air—water vapor curve is practically the same as that of the dry air curve at the same pressure. Therefore, water vapor evidently produces no decided effect upon the natural ionization in

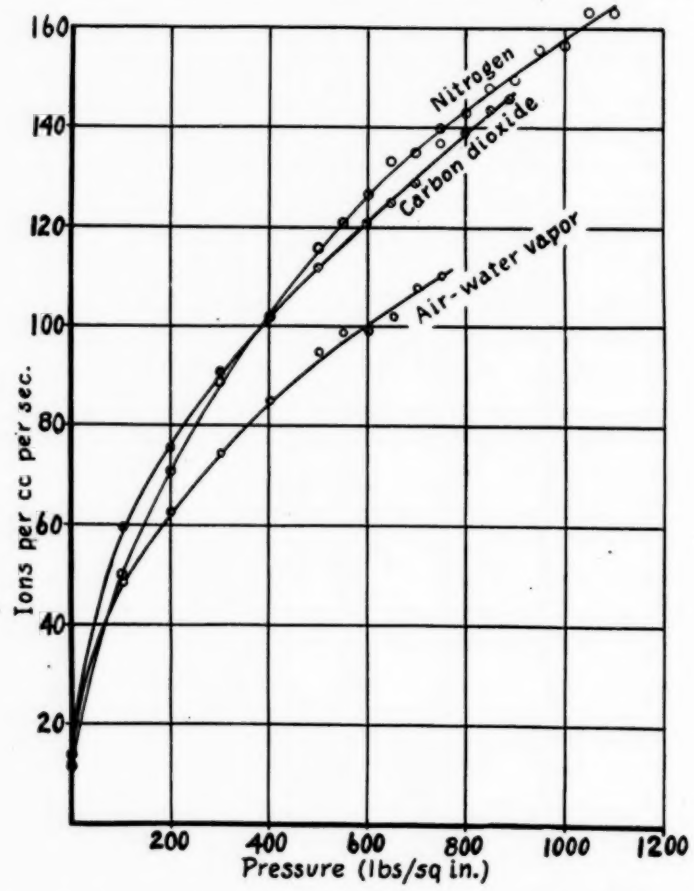

FIG. 5. Variation with pressure of the natural ionization in N_2, CO_2 and air saturated with water vapor.

aged, dust-free air. It might, however, produce a considerable effect in the presence of dust particles.

Since no outstanding differences other than those mentioned above were found to exist among the values of the natural ionization or the P-n curves obtained for the various gases investigated, there evidently

exists no special "anomalous" effect for nitrogen so far as this investigation is concerned. There remain, however, the larger slopes for nitrogen and carbon dioxide.

Effect of Lining

The effects of the metals constituting the ionization chambers, upon the natural ionization in gases, particularly air, were early investigated by several experimenters,[9] especially by Campbell and McLennan. These investigations, however, were ordinarily carried out at atmospheric pressure. Evidence has been provided to show that the natural ionization does depend upon the material constituting the vessel, and also upon the particular sample of the material.

In Figs. 3 and 4 are the three P-n curves which were secured with oxygen in ionization chambers of practically the same size (12 in. diameter) but with different metals constituting their inner surfaces. It is seen that the two curves for the respective cases in which the iron sphere was unlined and in which it was lined with copper, start at practically the same point and have practically the same initial and the same final slope. The early intermediate curvature is rather greater in the case of the copper lined sphere, however, resulting in considerably lower values for the ionization at high pressures in this case.

With the chamber lined with aluminum, the value of the ionization at atmospheric pressure was much larger than in the other two cases. This particularly high value of the ionization at atmospheric pressure appears to have been characteristic of the aluminum lining inasmuch as it was observed with each of the three spheres (see Fig. 4). The curvature of the curve for aluminum, however, corresponds very closely with that of the curve for the copper lining for pressures below 600 lbs. per sq. in. and is more persistent than in the latter curve at greater pressures. The result, therefore, is that the aluminum curve has a smaller final least slope than do the other two curves for oxygen in the 12 in. sphere, and the final absolute value of the ionization is larger than with the copper lining.

As is shown by Fig. 4, the curves obtained with each sphere lined with aluminum are very regular and correspond closely. It might be concluded, therefore, that the aluminum gave rise to a rather bounteous supply of comparatively easily absorbable radiation. This suggests

[9] A. Wood, Phil. Mag. **9**, 550 (1905);
N. R. Campbell, Phil. Mag. **11**, 206 (1906);
N. R. Campbell, Camb. Phil. Soc. Proc. **13**, 282 (1906);
J. C. McLennan, Phil. Mag. **14**, 760 (1907);
J. C. McLennan, Phys. Rev. **26**, 526 (1908).

an explanation in terms of the considerable secondary cathode radiation excited by gamma radiation in substances of light atomic weight.[10] The chief effect of the copper lining appears to have been the reduction of the absolute value of the ionization at high pressures. It should be noted that radiations from the iron which could have penetrated 1/16 in. of aluminum or copper would have affected the ionization occurring with these two linings.

Variation with Time

The variation with time of the natural ionization in the atmosphere is of interest in connection with problems concerned with the atmospheric potential gradient, the emanation content, the magnetic intensity, etc. Wood and Campbell,[11] McKeon,[12] Strong,[13] Wright,[14] Gockel,[15] Simpson,[16] Wulf,[17] Downey,[18] and others have investigated more or less exhaustively the variation with time of the natural ionization in air at atmospheric pressure. No general agreement appears to have resulted as to whether the diurnal variation is singly or doubly periodic or whether it exists at all.

In the present investigation of the variation at atmospheric pressure there was, as is designated by the dotted curves in Fig. 6, a decided similarity between fluctuations during the first two 24-hr. periods. The large general variations partook of a single periodicity with maxima in the early afternoon and minima in the early morning. The weather was turbulent or stormy during these periods. During the third period, when the sky was comparatively clear, the above periodicity did not appear. In view of previous work it is concluded that the present work, extending over a period of only 72 hrs., contributes very little toward the solution of the daily variation problem.

From the summary in Table II, it is seen that the average deviation from the mean at atmospheric pressure was of the order of ½ ion/cc sec., or about 5 percent of the mean, whereas the largest variations were of the order of 2 ions/cc sec., or about 20 percent of the mean. Smaller fluctuations were observed by Swann[19] in the same laboratory at about the same time.

[10] W. H. Bragg and J. P. V. Madsen, Phil. Mag. **15,** 663 (1908).
[11] A. Wood and N. R. Campbell, Phil. Mag. **13,** 265 (1907).
[12] T. F. McKeon, Phys. Rev. **25,** 399 (1907).
[13] W. W. Strong, Phys. Zeits. **9,** 117 (1908).
[14] C. S. Wright, Phil. Mag. **17,** 295 (1909).
[15] A. Gockel, Phys. Zeits. **10,** 845 (1909).
[16] G. C. Simpson and C. S. Wright, Roy. Soc. Proc. **A85,** 175 (1911).
[17] Benndorf, Dorno, Hess, v. Schweidler, Wulf, Phys. Zeits. **14,** 1141 (1913).
[18] K. M. Downey, Phys. Rev. **16,** 420 (1920).
[19] W. F. G. Swann, Jour. Franklin Inst. Oct. (1925).

Curve I of Fig. 6 shows that with oxygen at a pressure of 800 lbs. per sq. in. there was no periodicity corresponding to that at atmospheric pressure. The magnitude of the average deviation from the mean was about twice that in air at atmospheric pressure, and the magni-

TABLE II

Variations over 24-hr periods of the natural ionization at constant pressure.

Press.	No. of Readings	Mean no. of ions/ cc sec.	Ave. dev. from mean	Max. dev. from mean
800 lbs./in.²	67	118.82	1.163	5.62
Atmos.	71	10.58	0.600	2.23
Atmos.	66	11.21	0.695	2.02
Atmos.	72	10.71	0.427	1.24

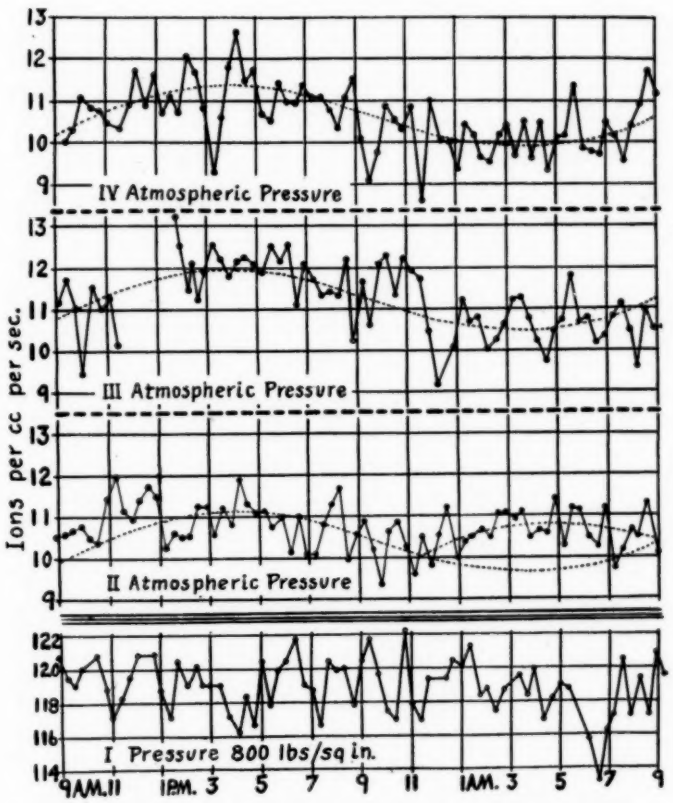
Ions per cc per sec.
IV Atmospheric Pressure
III Atmospheric Pressure
II Atmospheric Pressure
I Pressure 800 lbs/sq in.
9AM. 11 1PM. 3 5 7 9 11 1AM. 3 5 7 9

FIG. 6. Variation during 24-hr periods of the natural ionization in air at atmospheric pressure and at 800 lb./sq. in.

tude of the maximum deviation was rather more than twice the largest deviation at atmospheric pressure. The average deviation from the mean at a pressure of 800 lbs. per sq. in. was only about 1 percent and the maximum deviation about 5 percent of the mean. The larger

absolute values but the smaller fractional values of the variations occurring at the higher pressure may be explained in terms of fluctuations of soft radiations supposed to contribute to the total ionization.

Influence of Chemical Action

It has sometimes been suspected that chemical action might account for a part of the natural ionization in gases. With this possibility in mind, observations of the natural ionization occurring in air contained at atmospheric pressure in the 12 in. sphere were made before and after the admission of small quantities of hydrogen which would be expected to combine to a slight extent with the oxygen in the air. Also, observations of the natural ionization occurring within the 12 in. sphere in which had been placed pieces of silver foil and which had been filled with oxygen to atmospheric pressure were made before and after the admission of small quantities of hydrogen sulphide and also other quantities of silver.

In common with previous results,[20] those of the present investigation were negative so far as the detection of the dependence of the natural ionization in gases at atmospheric pressure upon slow chemical action is concerned. In certain cases there appeared to be slight increases in ionization at times coincident with increased chemical action. When the ionization values were plotted against the time, however, it was seen that there was practically no justification for the conclusion that the natural ionization was affected by the slow chemical action which resulted upon the admission of the different materials. That chemical action did occur upon admission of the hydrogen sulphide was evidenced by the tarnished condition of the silver and the brass parts of the apparatus subsequently observed.

In conclusion, the writer wishes to express his appreciation of the very general cooperation of the Physics faculty at Yale University where the experimental work was completed, and of the particularly kindly interest of Professor John Zeleny. Thanks are extended to Mr. C. J. Pietenpol who assisted in taking some of the readings, and to Professor W. B. Pietenpol for reading this paper. Finally, the writer desires to acknowledge his especial indebtedness to Professor W. F. G. Swann who suggested this research and who offered many helpful suggestions during the progress of the work.

Hale Physical Laboratory,
University of Colorado,
January 16, 1926.

[20] K. H. Kingdon, Phil. Mag. **32**, 396 (1916).
N. R. Campbell, Phil. Mag. **9**, 545 (1905).

TRANSITION PROBABILITIES: THEIR RELATION TO THERMIONIC EMISSION AND THE PHOTO-ELECTRIC EFFECT

By Ernest O. Lawrence*

Abstract

Assuming (a) Wien's formula for black body radiation, (b) that electrons ejected thermally from a hot body have the experimentally known Maxwell distribution of velocities, and (c) that photo-electric emission from a solid surface is independent of the temperature of the solid, a theory is developed which leads directly to Richardson's thermionic current equation without importing into the argument circumstances not realized in experiment or assumptions and approximations that can be questioned. Detailed consideration of the mechanism of emission and absorption along the lines of Einstein's derivation of Planck's radiation formula leads to the same expression for the ratio of absorption to emission B_ν/q_ν obtained in other theories based on application of the principle of detailed balancing of processes occurring in systems in equilibrium. It is thus shown that observed photo-electric and thermionic phenomena from solid surfaces may be regarded as experimental confirmations of expressions B_ν/q_ν deduced in such theories.

AMONG the theories developed to account for thermionic phenomena are those which regard the emission of electrons from hot bodies as a photo-electric effect connected with the associated temperature radiation.[1] This view of the matter is in formal harmony with the ideas underlying Einstein's derivation of Planck's formula. Inasmuch as these theories, for example, Richardson's theory of the so-called "complete photo-electric emission," lead to an expression for the relative efficiencies of light of various frequencies in ejecting electrons from a metal surface, they are intimately related to more recent theories designed to evaluate transition probability coefficients, notably those of Kramers,[2] Milne[3] and Becker[4]. Richardson's theory was developed by statistical and thermodynamical considerations of a system of free electrons in equilibrium with an adjacent hot body and necessitated assumptions and approximations which were open to question, as indeed, the author of the theory indicated. In the present paper an attempt is made to deduce from experimentally recognized assumptions the probability of photo-electric emission from a solid

* National Research Fellow.

[1] Richardson, "Emission of Electricity from Hot Bodies," p. 110.

[2] Kramers, Phil. Mag. **46**, 836 (1923).

[3] Milne, Phil. Mag. **47**, 209 (1924).

[4] Becker, Zeits f. Physik **18**, 325 (1923).

surface as a function of the frequency of the light. The probability, so calculated, is then applied to a new derivation of the ratio of the probabilities of absorption and emission B_ν/q_ν, a ratio which has been obtained in the theories mentioned above by application of a principle of detailed balancing to a system in equilibrium.

It is our purpose to avoid the necessity of invoking circumstances not realized or assumptions that are not directly verified experimentally and we shall start with two universal properties of matter now well established. First, we have the spectral energy distribution I_ν of the radiation associated with the temperature T as represented by Wien's expression for high frequencies,

$$I_\nu = 8\pi h\nu^3 C^{-3} e^{-h\nu/kT} \tag{1}$$

and secondly the distribution of velocities of the electrons emitted thermally from a body at temperature T, viz.,

$$n_w = N(T) w^3 e^{-mw^2/2kT} dw \tag{2}$$

where n_w is the number emitted per second with speeds in the range w, $w+dw$. It is to be noted that $N(T)$ is a function of T only and w comes in as a factor raised to the third power instead of squared because the number emitted per second is proportional to the velocity and the Maxwellian distribution. The fact that these two properties are common to all kinds of matter suggests a close relationship and we shall adopt the plausible hypothesis that the electrons are ejected photo-electrically by the temperature radiation. This hypothesis is in strict harmony with the viewpoints of the more recent theories mentioned above. Now the number of electrons n_ν ejected by radiation of frequencies between ν and $\nu+d\nu$ will be proportional to the intensity $I_\nu d\nu$ and the probability $f(\nu)$ of unit intensity ejecting an electron, that is,

$$N_\nu = f(\nu) I_\nu d\nu \tag{3}$$

This relation may be simply regarded as defining $f(\nu)$. Further, it is well known that the velocity of the photo-electrons w produced by radiation of frequency ν is given by,

$$\tfrac{1}{2} m w^2 = h(\nu - \nu_0) \tag{4}$$

where ν_0 is the smallest frequency able to eject photo-electrons from the surface—the threshold frequency.

On the basis of our hypothesis it follows from (2) and (4) that the number emitted per second by frequencies ν, $\nu+d\nu$ is

$$n_\nu = 2N(T)(h/m)^2(\nu-\nu_0) e^{-h(\nu-\nu_0)/kT} d(\nu-\nu_0) \tag{5}$$

In view of (1) on equating (3) and (5) we have

$$f(\nu)=\frac{hc^3}{4\pi m^2}N(T)e^{h\nu_0/kT}\frac{(\nu-\nu_0)}{\nu^3} \tag{6}$$

Experiments have demonstrated that photo-electric effects are independent of the temperature of the radiated body so that this probability function is independent of the temperature. Because of the presence of the factor $e^{h\nu_0/kT}$ in the expression we deduce as a consequence thereof that

$$N(T)=\alpha e^{-h\nu_0/kT} \tag{7}$$

where α is a constant.

Thus we conclude that the magnitude of the photo-electric emission from a solid surface when illuminated by unit intensity of frequency ν is

$$f(\nu)=\frac{\alpha hc^3}{4\pi m^2}\frac{(\nu-\nu_0)}{\nu^3}$$

That this is the correct law of variation of the photo-electric effect from solid surfaces has been verified in several instances. Richardson obtained a similar expression and the experiments of K. T. Compton and Richardson[5] were the first to show that, as the formula predicts, light of frequency 3/2 of the threshold value is the most efficient in the production of a photo-electric effect. Later Souder[6] obtained confirmative data of possibly greater precision. Finally should be mentioned the experiments of Wilson[7] who observed the variation of the photo-electric effect from a sodium surface when illuminated by radiation from a black body at various temperatures. As will be seen below, this probability function implies that the photo-electric currents thus observed should vary with the temperature of the black body according to Richardson's thermionic equation. Wilson's experiments confirmed this implication.

The total thermionic current i may be deduced readily as a function of the temperature and threshold frequency, for clearly it is,

$$i=\int_0^\infty N_w\epsilon\, dw$$

[5] K. T. Compton and O. W. Richardson, Phil. Mag. **26**, 549 (1913).
[6] Souder, Phys. Rev. **8**, 310 (1916).
[7] Wilson, Proc. Roy. Soc. **A93**, 359 (1917).

From (2) and (7) we have, therefore,

$$i = \epsilon\alpha e^{-h\nu_0/kT} \int_0^\infty w^3 e^{-mw^2/2kT} dw$$

$$= AT^2 e^{-b/T}, \qquad b = h\nu_0/k$$

which is Richardson's thermionic equation. Thus we have correlated the facts of thermionics and the photo-electric effect without invoking a system in thermodynamic equilibrium and, except for the hypothesis that thermionic emission is a pho o-electric effect, our assumptions are experimental facts.

Now Milne obtains from thermovdnamical considerations and the principle of detailed balancing* the ratio B_ν/q_ν for optical frequencies, where B_ν is the probability that an electron in the normal energy level will be raised to a higher energy state when in the presence of unit light intensity of frequency ν and q_ν is the effective collision-capture area of an atom capable of capturing an electron in the higher state, thereby reducing it to its normal condition.

The significance of the probability function $f(\nu)$ as defined above is quite distinct from that of the transition probability coefficient B_ν of Milne's theory for, clearly, $f(\nu)$ is proportional to the probability that an electron will be raised from a given stationary state to one of higher energy and, before recombining, escape from the surface. However, having ascertained $f(\nu)$ we are able to deduce the ratio B_ν/q_ν. The following analysis makes this clear.

Consider an annular volume element $d\tau$ of a metal relative to an element dA of its surface, i. e.,

$$d\tau = 2\pi r^2 \sin\theta \, d\theta \, dr$$

where r is the distance of any portion of $d\tau$ from dA. The number of electrons raised from the normal state to a free state of higher energy per unit time in $d\tau$ by absorption of light of frequency ν, $\nu+d\nu$ and intensity $I_\nu d\nu$ is, according to Milne's theory,

$$N \, d\tau B_\nu I_\nu d\nu$$

where N is the number of electrons in the normal configuration per unit volume. Of this number there will be a portion $dA\cos\theta/4\pi r^2$ which have velocities such as to cause them to pass through the ele-

* It may be remarked parenthetically that the principle of detailed balancing is simply that in a system in equilibrium the number of elementary processes occurring in a forward direction in unit time is equal to the number in the reverse direction.

ment of surface dA if they are not absorbed in their passage thereto. But we further recognize that of the number in the higher state there will always be a certain portion dn that will be absorbed again in time dt, i. e.,

$$-dn = A_{,n}\, dt$$

where $-dn$ is the number absorbed of a group n in time dt. Thus integrating we have,

$$n = n_0 e^{-A_{,}t}$$

where n is the number unabsorbed after a time t of a group n_0 existing at $t=0$. Clearly the time taken for an electron to pass from the annular volume element $d\tau$ to the surface element is

$$t = r/w$$

In view of these considerations we have that the total number reaching dA per unit time which have been raised from the normal state to the higher energy value by radiation of frequency $\nu,\nu+d\nu$ is

$$i_{,}dA = \frac{1}{2} N dA B_{,} I_{,} d\nu \int_0^{\pi/2} d\theta \int_0^{\infty} dr \sin\theta \cos\theta\, e^{-A_{,}r/w}$$

which reduces to

$$i_{,} = \frac{1}{2} N I_{,} d\nu \frac{w}{A_{,}} B_{,} \tag{8}$$

Now we have shown that the magnitude of the emission from a surface by light of frequency ν, $\nu+d\nu$ and intensity $I_{,}d\nu$ is

$$i_{,} = \frac{\nu-\nu_0}{\nu^3} I_{,} d\nu \times \text{constant} \tag{9}$$

From (8) and (9) therefore we have that

$$\frac{w}{A_{,}} B_{,} = \frac{\nu-\nu_0}{\nu^3} \times \text{constant}$$

which may be written in the form

$$\frac{B_{,}}{q_{,}} = \frac{\nu-\nu_0}{\nu^3} \times \text{constant}$$

where

$$q_{,} = \frac{A_{,}}{w} \times \text{constant}$$

is the effective "collision-capture area" of an atom relative to a ν-electron.

Thus by a procedure quite distinct from the method of detailed balancing of the processes occurring in a system in complete equilibrium we have obtained the ratio of absorption to emission, B_ν/q_ν.

In this connection it should be emphasized that the probability of absorption A_ν and the effective collision area q_ν do not refer to a process involving the return of the electron to the normal state in the atom but to any state that prevents its escape from the surface. In Milne's theory the effective collision area concerns the capture of an electron wherein it is returned to the same stationary state from which it was ejected by the light of frequency ν. The similarity of the present expression B_ν/q_ν with the analagous ratios in theories based on the principle of detailed balancing suggests that the probability of capture and return to a state other than the normal one is the same function of the frequency as, or negligible in comparison to, the probability of return to the normal state. Of course we have implicitly regarded elastic impacts of the electrons with atoms as of no importance in the calculations.

Having obtained the ratio of the probabilities of absorption B_ν and emission q_ν various attempts have been made to evaluate the absorption probability B_ν by determining the nature of the emission q_ν with the ultimate end in view of a comparison with experiment. In the optical region the outstanding experiments on such absorption probabilities are the very interesting experiments of Foote, Mohler and Chenault[8] on the photo ionization of caesium vapor and also there is Lawrence's[9] observation of the variation with the frequency of the photo-electric effect in rapidly distilling potassium vapor. The absorption in caesium vapor was observed to decrease rapidly from the series limit to higher frequencies in a manner not in accord with any theoretically determined B_ν, while the experiments with the jet of potassium vapor revealed that the absorption increased from a threshold value ν_0 to higher frequencies over the range investigated according to the law*

$$B_\nu' = \frac{(\nu-\nu_0)^{3/2}}{\nu^3} \times \text{constant}$$

[8] Mohler, Foote and Chenault, Phys. Rev. **27**, 37 (1926).

[9] Lawrence, Phil. Mag. **50**, 345 (1925).

* This law was deduced from the data of Fig. 3 (above reference) assuming that the potassium photo-cell used to measure relative light intensities was selective according to the function $f(\nu)$ deduced in the present paper.

a variation with frequency also in disaccord with all theoretically evaluated expressions for B_ν. Now, therefore, it is interesting to point out that, on the basis of the deductions herein given, *thermionic and photo-electric phenomena observed from solid surfaces may be regarded as experimental confirmations of the ratio B_ν/q_ν evaluated in statistical equilibrium theories.*

It is an especial pleasure to acknowledge my indebtedness to Professor W. F. G. Swann and Professor Leigh Page.

SLOANE LABORATORY,
YALE UNIVERSITY,
February 17, 1926.

THE ABSORTION SPECTRA OF TELLURIUM, BISMUTH, CHROMIUM AND COPPER VAPORS IN THE VISIBLE AND ULTRAVIOLET

By R. V. Zumstein

Abstract

Using a hot carbon tube at about 1600°C as the absorption cell, the spectra of these elements have been studied in absorption from 6000 to 2000A. The vapor of tellurium was dissociated into atoms by a simple device and 4 absorption lines were found. Two new arc lines were measured. The same arrangement gave 8 bismuth absorption lines, 4 being new. These are exactly the lines to be expected from the work of Ruark, Foote, Mohler and Chenault. Four new arc lines were measured in the spectrum of a 75 ampere arc. Chromium was placed directly in the carbon tube and 3 triplets were absorbed. Nineteen copper lines were absorbed, 10 being from the normal state in agreement with Shenstone and McLennan and McLay and 9 new ones from excited states.

THE absorption spectrum of tellurium vapor was investigated by Evans[1] at various pressures and temperatures. He found that if a small quantity of tellurium was gradually heated in an enclosed quartz tube, the vapor was opaque or showed absorption bands. As the vapor was heated, it became more transparent and the bands disappeared. At a temperature of about 1000°C and a sufficiently low pressure, the vapor was perfectly transparent from the visible to 2500A. His interpretation was that at low temperatures and high vapor pressures the molecules of tellurium vapor are composed of several atoms and that at high temperatures these molecules dissociate into atoms if the pressure is low so that there is slight chance of recombination.

Guided by Evans' experiments, I have modified the method used for manganese.[2] The tellurium was not placed directly in the carbon tube but in a small iron tube as shown in Fig. 1. C is the carbon tube heated by the torch T. The hottest part of the tube was at about 1600°C and the coldest at 800°C. Te is the tellurium in the small iron tube at about 500°C. Through a second tube N, a gentle stream of nitrogen flowed to displace the atmospheric oxygen from the tube. By this method four absorption lines were observed corresponding

[1] Evans, Astrophys. J. **36**, 228 (1912).
[2] Zumstein, Phys. Rev. **26**, 765 (1925).

to the arc lines 2385.793, 2383.268, 2259.02 and 2142.94. The first pair were sharp absorption lines but the last two were quite broad.

The tellurium arc for comparison was obtained by placing tellurium in the lower carbon of a 50 ampere arc. The spectrum so obtained was similar to that described by Uhler and Patterson.[3] To their list of 15 arc lines I would add a strong pair of reversed lines at 2001.87 and 1994.07. Their lines 2208.58, 2160.1 were observed as diffuse reversals and 2147.33, 2081.8 as sharp reversals. I have not been able to make any analysis of the tellurium arc spectrum beyond a guess that the lowest lying levels are rather widely separated p levels which would combine with s and d levels to give the sharp and diffuse lines observed in the arc spectrum. McLennan, Smith and Peters[4] have recently observed a group of tellurium arc lines in the near infrared.

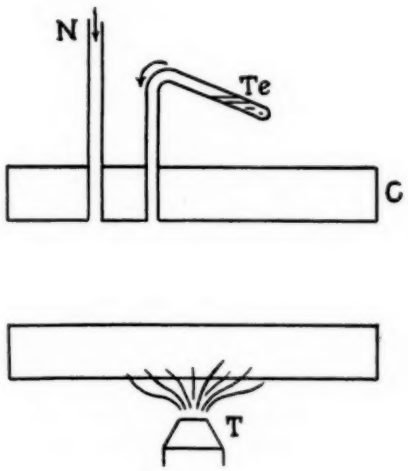

FIG. 1

Bismuth. Since some of the bismuth absorption lines appeared while studying the absorption spectrum of tellurium vapor, it seemed worth while to repeat the experiments with pure bismuth using the arrangement of Fig. 1. The 8 absorption lines observed are given in Table I. The first four of these lines were observed in absorption by Ruark, Mohler, Foote and Chenault.[5] They state that a band absorption extended from 2205A to the shorter wave-lengths. It may be that these bands were due to bismuth molecules which were dissociated in the present experiments. All of the absorptions are from the state

[3] Uhler and Patterson, Am. Journal of Science **186,** 135 (1913).
[4] McLennan, Smith and Peters, Trans. Roy. Soc. Canada, III, **39** (1925).
[5] Ruark, Mohler, Foote and Chenault, B. S. Sci. Papers, **19,** 484 (1924).

called $3d_2$ by Ruark, etc., and afford very good support of the analysis of the bismuth arc spectrum which they give.

A bismuth arc of 70 amperes gives an intense continuous spectrum extending from the visible to 1900A with the bismuth arc lines reversed. I have compared this arc with that given by Ruark, etc. between 2075 and 2000A. Their lines 2020.5, 2068.99 and 2073.2 were not observed and are perhaps not arc lines. Four new lines were found namely: 2064.4 (2*R*), 2057.4 (2*R*), 2041.8 (2*R*) and 2041.6 (2*R*). The difference in frequency of 2041.8 (48960) and 2582.1 (38718) equals $3d_1{}^B - 3D_1{}^A$. Also the frequency difference of 2041.6 (48964) and 2224.2 (44946)

TABLE I

Bismuth absorption spectrum

λ(I.A.)	Intensity 70 amp. arc	Intensity Absorption	Series notation
3067.732	10R	10	$3d_2-\alpha$
2276.578	6R	5	$3d_2-\delta$
2230.626	10R	10	$3d_2-\epsilon$
2228.240	8R	9	$3d_2-\zeta$
2177.33*	3R	2	$3d_2-\eta$
2110.263*	8R	6	$3d_2-\theta$
2061.73*	10R	9	$3d_2-\iota$
2020.99*	3R	2	$3d_2-\kappa$

* New absorption lines

equals $3d_1{}^B - 3D_2$. This enables us to classify these four bismuth lines and to evaluate two terms 2490 and 2486 which resemble several other bismuth terms in being a close pair. A classification of the bismuth arc spectrum has also been given by Kopferman[6] who indicates that 2582.1 comes from $3d_1{}^B$ which cannot be correct as it is not reversed and also from $3D_2$ which is possible.

Chromium. The absorption spectra of chromium and copper vapors were investigated by placing a piece of the metal in the carbon tube and heating it directly to about 1600°C. The method was the same as that used for manganese.[2] Three chromium triplets were observed in absorption as shown in Table II. The first two triplets had been previously observed in absorption by Grotrian and Gieseler[7] and by McLennan and McLay.[8] In fact these nine lines and many others were obtained in the chromium absorption spectrum by King[9]. In King's experiments, the vapor was at only one temperature, 2600°C. He

[6] H. Kopfermann, Zeits. f. Physik **21**, 322 (1924).
[7] W. Grotrian and H. Gieseler, Zeits. f. Physik **22**, 245 (1924).
[8] McLennan and McLay, Trans. Roy. Sco. Canada, **III**, 89 (1925).
[9] A. S. King, Astrophys. J. **60**, 291 (1924).

obtained absorptions from the normal state and from some of the excited states. It is not therefore obvious from his results that the triplet 2366, 2365, 2364 are transitions to the normal state which does follow from the present experiments. The threefold ^7p term defined by this triplet should combine with the 5^7s term (see Gieseler's article on the arc spectrum of chromium[10]) to give a triplet in the infrared of wave-lengths 18716, 18661, 18585A. Randall and Barker[11] found a chromium triplet at 18717.0 ($I=20$), 18654.2 (30), 18583.5 (30). The agreement appears to be satisfactory.

TABLE II

Chromium absorption spectrum

λ(I.A.)	ν	Series
4289.726	23304.98	4^7s-4^7p
74.802	386.34	
54.341	498.81	
3605.330	27728.83	4^7s-4^7p
593.483	820.24	
78.688	935.25	
2366.85	42237.5	4^7s-5^7p
65.96	53.3	
64.74	75.1	

Copper. It seemed desirable to repeat my former experiments on the absorption of copper vapor,[12] using the large Hilger spectroscope, size E_1, which is now available. Shenstone,[13] McLennan and McLay,[8] and Stücklen[14] have recently studied this problem. Shenstone gives evidence for a pair of metastable states (one is the X term introduced by Randall[15]) which are not far removed from the normal state ($\Delta\nu=$ 13245.4 and 11202.5).

With the copper vapor at about 1200°C, I obtain a series of absorption lines which appear to come from copper atoms in the normal state. When the temperature is increased to 1600°C, most of these lines increase in width and a group of faint absorption lines appear which I think are due to copper atoms in excited states. These two groups are given in Table III.

All of the absorption lines from the normal state were obtained by Shenstone and by McLennan and McLay. The three lines 2492, 2441

[10] H. Gieseler, Zeits. f. Physik **22**, 243 (1924).
[11] Randall and Barker, Astrophys. J. **49**, 58 (1919).
[12] Zumstein, Phys. Rev. **25**, 523 (1925).
[13] Shenstone, Phil. Mag. **49**, 952 (1925).
[14] Stücklen, Zeits. f. Physik **33**, 562 (1925).
[15] Randall, Astrophys. J. **34**, 1 (1911).

and 2244 were narrow absorption lines at the highest temperature. The remainder from the normal state widen out with increase of temperature. All of the absorption lines from the metastable states were sharp. The narrow pair, 2199.73 and 2199.57 were observed as two reversals in the arc as noted by Shenstone and Stücklen. They were absorbed as two narrow absorption lines by the vapor. At high temperatures a group of absorption bands appeared from 2275 to 2228A as found by Stücklen in the copper spark under water. Because of these bands, one cannot be certain if there was faint absorption at some of the arc lines in this region. By changing the inductance and

TABLE III

Copper absorption spectrum

Wave-lengths from normal state	Wave-lengths from excited state
3273.976	5105.551*
3247.550	2392.629* very faint
2492.142 sharp	2293.832*
2441.625 sharp	2230.071*
2244.240 sharp	2227.74*
2225.665	2215.65* very faint
2181.68	2214.56*
2179.91	2199.73*
2165.06	2199.57*
2024.3	

* New absorption lines

capacity of the circuit of the under water spark, Stücklen obtained a group of copper arc lines which were considered to come from the normal state. The grouping so obtained is considerably different from that afforded by the more direct method of heating the vapor in a tube with a torch.

The present experiments show very clearly that the copper atom has one or more metastable states which differ in frequency from the normal state by about 10,000 cm^{-1}. They do not show the exact value of this difference. In the copper arc spectrum, there are pairs in the visible and near ultraviolet having the frequency difference of 248.4, which is that of the two lines 3274 and 3247. If any of these pairs should show the faint absorption corresponding to the metastable states, then we can evaluate with certainty the terms which correspond to the metastable states. According to Shenstone's work, we should expect that the green line 5105 would be absorbed and at slightly higher temperature the yellow pair 5782. and 5700. I have frequently studied the copper absorption in the visible but always with negative results. Recently we have received from A. Hilger and Co. a glass

prism and lens to fit their E_1 quartz spectrograph. Having available therefore a dispersion of 12A per mm at 5700 A,I have returned to the problem and find that in the visible spectrum only the green line 5105 is faintly absorbed at the highest temperatures. The fact that the yellow pair was not absorbed is not an argument against Shenstone's work because the absorption of the green line 5105 was only observed on a small fraction of the plates taken. To obtain the yellow pair in absorption would require a still higher temperature.

NATIONAL RESEARCH FELLOWSHIP,
PHYSICS DEPARTMENT,
UNIVERSITY OF MICHIGAN,
February 13, 1926.

THE QUANTUM THEORY OF THE DIELECTRIC CONSTANT OF HYDROGEN CHLORIDE AND SIMILAR GASES

By Linus Pauling*

Abstract

The quantum theory of diatomic dipoles.—Using the treatment of Pauli, an expression for the dielectric constant of a diatomic dipole gas is obtained, in which half-quantum numbers are used. It is shown that for cases of practical interest the approximation suggested by Pauli is not valid; hence numerical values of the temperature-function C have been calculated and tabulated.

Application to experimental measurements.—The theory has been applied in the interpretation of Zahn's measurements of the dielectric constants of the hydrogen halides. The electric moments of molecules of hydrogen chloride, bromide, and iodide were found to be 0.3316, 0.252, and 0.146×10^{-18} cgsu respectively; i.e., only about one-third of the values given on the basis of the classical theory. Moreover, the values 0.00077 and 0.00102 for $4\pi N_0\alpha$ for hydrogen chloride and bromide, in which α is the coefficient of induced polarization, are shown to be in better agreement with measurements of indices of refraction than are the classical theory values. A discussion is given of possible inaccuracies in the theory, of the choice of quantum numbers, and of the possibility of weak quantization.

Introduction

Under the influence of an electric field a gas whose molecules have a permanent electric moment and in addition can have a further moment induced in them by deformation becomes polarized in the direction of the field, the amount of polarization per unit volume being[1]

$$P=\frac{3}{4\pi}\,\frac{\epsilon-1}{\epsilon+2}F=N\mu\,\overline{\overline{\cos}}\,\theta+N\alpha F\,, \qquad (1)$$

in which ϵ is the dielectric constant of the gas, F the strength of the applied field, N the number of molecules in unit volume, μ the permanent electric moment of a molecule, and α the coefficient of induced polarization of a molecule. $\overline{\overline{\cos\theta}}$ is the average value of $\overline{\cos}\,\theta$ for all molecules in the gas, and $\overline{\cos\theta}$ is the time-average of $\cos\theta$ for one molecule in a given state of motion, θ being the angle between the axis of the electric dipole and the lines of force of the applied field.

An expression for $\overline{\overline{\cos\theta}}$ applicable to polyatomic molecules in general was obtained by Debye[2] with the use of classical statistical mechanics.

* National Research Fellow in Chemistry.

[1] See, for example, Debye in Marx "Handbuch der Radiologie," Leipzig Akademische Verlagsgesellschaft, 6, 619 (1925).

[2] P. Debye, Phys. Zeits. 13, 97 (1912).

From the Maxwell-Boltzmann distribution law the probability that the axis of the electric dipole in the molecule will lie between the angles θ and $\theta+d\theta$ with the lines of force is

$$\frac{e^{\mu F\cos\theta/kT}\sin\theta\,d\theta}{\int_0^\pi e^{\mu F\cos\theta/kT}\sin\theta\,d\theta},$$

and the average value of $\cos\theta$ is

$$\overline{\cos\theta}=\frac{\int_0^\pi e^{\mu F\cos\theta/kT}\cos\theta\sin\theta\,d\theta}{\int_0^\pi e^{\mu F\cos\theta/kT}\sin\theta\,d\theta}. \tag{2}$$

This expression becomes on integration the Langevin function,

$$L\left(\frac{\mu F}{kT}\right)=\coth\frac{\mu F}{kT}-\frac{kT}{\mu F},$$

which reduces for values of μF small in comparison with kT to

$$\overline{\cos\theta}=\frac{1}{3}\frac{\mu F}{kT}. \tag{3}$$

This result must now, however, be replaced by one based upon the quantum theory. In this case a generally applicable expression cannot be obtained, and it is necessary to consider particular molecular models. The simplest of these, the diatomic molecule for which the axis of the electric dipole coincides with the line joining the nuclei of the two atoms, is believed to represent the hydrogen halides, for which data are available to make possible the evaluation of their electric moments.

The Quantum Theory of the Diatomic Dipole

The dielectric constant of diatomic dipole gases has been treated on the basis of the quantum theory by W. Pauli, Jr.,[3] whose treatment forms the basis of the following discussion.

The Hamiltonian function for the motion of a diatomic dipole in an electric field, using polar coordinates with the polar axis in the direction of the lines of force, is

$$H=\frac{1}{2I}\left(p_\theta^2+\frac{p_\varphi^2}{\sin^2\theta}\right)-\mu F\cos\theta, \tag{4}$$

[3] W. Pauli, Jr., Zeits. f. Physik **6**, 319 (1921).

in which p_θ and p_ϕ are the momenta corresponding to the coordinates θ and φ, and I is the moment of inertia of the rotator about an axis through its center of mass and normal to the lines joining the atomic nuclei. The coordinate φ is cyclic, and p_ϕ is accordingly constant. Applying the Wilson-Sommerfeld quantum conditions we write

$$\oint p_\theta d\theta + \left| \oint p_\varphi \, d\varphi \right| = mh \tag{5}$$

and

$$\oint p_\varphi \, d\varphi = 2\pi p_\varphi = nh, \tag{6}$$

in which m and n are the two quantum numbers describing the condition of motion of the rotator. Introducing (6) and the relation $p_\theta = I\dot{\theta}$ in (4), there is obtained the differential equation

$$dt = \frac{2\pi I \, d\theta}{\sqrt{8\pi^2 IW - \frac{n^2h^2}{\sin^2\theta} + 8\pi^2 I\mu F \cos\theta}}, \tag{7}$$

in which W is the energy-constant. The time-average value of $\cos\theta$ for a rotator in a given state of motion is, then,

$$\overline{\cos\theta} = \frac{\oint (8\pi^2 IW - \frac{n^2h^2}{\sin^2\theta} + 8\pi^2 I\mu F \cos\theta)^{-\frac{1}{2}} \cos\theta \, d\theta}{\oint (8\pi^2 IW - \frac{n^2h^2}{\sin^2\theta} + 8\pi^2 I\mu F \cos\theta)^{-\frac{1}{2}} \, d\theta}. \tag{8}$$

If μF is very small in comparison with the total energy W these expressions may be expanded in powers of μF and terms higher than linear neglected; it is, moreover, permissible to substitute for W the value $W_0 = m^2h^2/8\pi^2 I$ corresponding to zero field. Upon evaluating the resultant integrals by contour integration there is obtained the expression

$$\overline{\cos\theta} = \frac{4\pi^2 \mu F I}{m^2h^2}\left(\frac{3}{2}\frac{n^2}{m^2} - \frac{1}{2}\right). \tag{9}$$

Pauli assigned to m values $1, 2, 3, \cdots \infty$, and to n $\pm 1, \pm 2, \pm 3, \cdots \pm m$. We shall give m the values $1/2, 3/2, 5/2, \cdots \infty$, and n $\pm 1/2, \pm 3/2, \pm 5/2, \cdots \pm m$; for these half-quantum numbers for m are indicated by the infra-red oscillation-rotation absorption spectrum[4]

[4] Colby, Astrophys. J. 58, 303 (1923).

of hydrogen chloride and definitely required by the recently observed[5] pure rotation absorption spectrum. The choice of values for n will be discussed later. Assigning equal *a priori* probabilities to all of the possible quantum states characterized by half-integral values of m and n we have for the probability of a given state

$$\omega(m,n)=\frac{e^{-W/kT}}{\sum_{m=\frac{1}{2}}^{\infty}\sum_{n=-m}^{+m}e^{-W/kT}}. \tag{10}$$

Introducing the variable $\sigma=\Theta/T=h^2/8\pi^2IkT$ we obtain the following expression for $\overline{\cos\theta}$:

$$\overline{\cos\theta}=\frac{\mu F}{kT}\,\frac{1}{2\sigma}\,\frac{\sum_{m=\frac{1}{2}}^{\infty}\sum_{n=-m}^{+m}\frac{1}{m^2}\left(\frac{3}{2}\,\frac{n^2}{m^2}-\frac{1}{2}\right)e^{-\sigma m^2}}{\sum_{m=\frac{1}{2}}^{\infty}\sum_{n=-m}^{m}e^{-\sigma m^2}}. \tag{11}$$

Pauli, who obtained a similar expression with whole quantum numbers, evaluated the sums by assuming σ to be very small. This is not justifiable, however, for it leads to results in error by 30 percent or more in cases of practical interest, for which σ has values near 0.05. Replacing m by $r-\frac{1}{2}$ and n by $s-\frac{1}{2}$ and summing for s one obtains

$$\overline{\cos\theta}=\frac{\mu F}{kT}C, \tag{12}$$

where

$$C=\frac{1}{4\sigma}\,\frac{\sum_{r=1}^{\infty}\frac{r}{(r-\frac{1}{2})^3}e^{-\sigma(r-\frac{1}{2})^2}}{\sum_{r=1}^{\infty}re^{-\sigma(r-\frac{1}{2})^2}}. \tag{13}$$

For very large values of σ; i. e., for very low temperatures, C is equal to $2/\sigma$. As σ tends to zero C approaches asymptotically the value 4.570, for $\sum_{r=1}^{\infty}\frac{r}{(r-\frac{1}{2})^3}e^{-(r-\frac{1}{2})^2}$ approaches $\sum_{r=1}^{\infty}\frac{r}{(r-\frac{1}{2})^3}$, which has the value 9.140, and $\sum_{r=1}^{\infty}re^{-\sigma(r-\frac{1}{2})^2}$ can be replaced by the integral $\int_0^{\infty}re^{-\sigma(r-\frac{1}{2})^2}\,dr$, which is equal to $1/2\sigma$. C has been determined for intermediate values of σ by numerical substitution, from five to twenty-

[5] Czerny, Zeits. f. Physik 34, 227 (1925).

five terms being used in order that the final figure might be accurate to 0.05 percent. The results of the calculations are given in Table I.

TABLE I

σ	C	σ	C
Very large	$2/\sigma$	0.05	3.599
1.00	1.578	.04	3.690
0.20	2.848	.03	3.796
.10	3.264	.02	3.929
.07	3.445	0.00	4.570

CONSIDERATION OF EXPERIMENTAL RESULTS

Substituting (12) in (1), we obtain

$$\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2}=N\frac{\mu^2}{kT}C+N\alpha\,, \tag{14}$$

in which C is a function of the temperature. This property differentiates this result from those of Debye and Pauli, who obtained for C the constant values 1/3 and 1.5367 respectively. Since for gases $\epsilon+2$ is approximately 3, we may write

$$(\epsilon-1)T=4\pi N\frac{\mu^2}{k}C+4\pi N\alpha T\,. \tag{15}$$

The equations of Debye and Pauli require that a plot of $(\epsilon-1)_0T$, in which the subscript 0 indicates that the dielectric constant is that of the gas at constant density (that at standard conditions), against T be a straight line; the calculations given in this paper, on the other hand, require the curve to deviate from a straight line, since C is found not to be a linear function of the temperature. Moreover, α and $4\pi N\alpha$ will have one value when obtained from measurements of ϵ with the use of the equation of Debye or of Pauli, and a different value if our calculations are used.

The only extensive measurements of the dielectric constants of diatomic dipole gases are those of Zahn[6] on hydrogen chloride, bromide, and iodide. Values of Θ for these gases are obtained in the interpretation of their infra-red spectra. Czerny[5] gives for hydrogen chloride the value 10.397 for $hc/8\pi^2I$, which leads to $\Theta=14.9°$ for this gas. An equally accurate value for hydrogen bromide is not at hand, for its pure rotation spectrum has not been observed. Kratzer[7] gives for I the value 3.258×10^{-40} g. cm^2, from oscillation-rotation spectra, corresponding to Θ12.15°. Since Kratzer's value $I=2.594\times10^{-40}$g.cm^2 for hydrogen chloride corresponds to $\Theta=15.09°$, which is slightly high,

[6] Zahn, Phys. Rev. **24**, 400 (1924).

[7] Kratzer, Zeits. f. Physik **3**, 289 (1920).

I have used for hydrogen bromide the value $\Theta = 12.0°$. No spectral data for hydrogen iodide have been obtained; from a consideration of atomic sizes obtained from crystal structure data I have predicted the approximate figures $I = 4.29 \times 10^{-40}$ g. cm^2 and $\Theta = 9.2°$ for this gas.

There are, then, two constants, μ and α, to be evaluated from the experimental data for each gas. These were determined in such a way as to cause the theoretical curve to pass through two experimental points, one at about 300° and one at about 500°A. The curves shown in Fig. 1 are obtained by placing $\mu = 0.3316 \times 10^{-18}$cgsu and $4\pi N_0\alpha = 0.00077$ for hydrogen chloride, and $\mu = 0.252 \times 10^{-18}$ and $4\pi N_0\alpha = 0.00102$ for hydrogen bromide; N_0 here represents the number of molecules per cc for the gas at standard conditions.

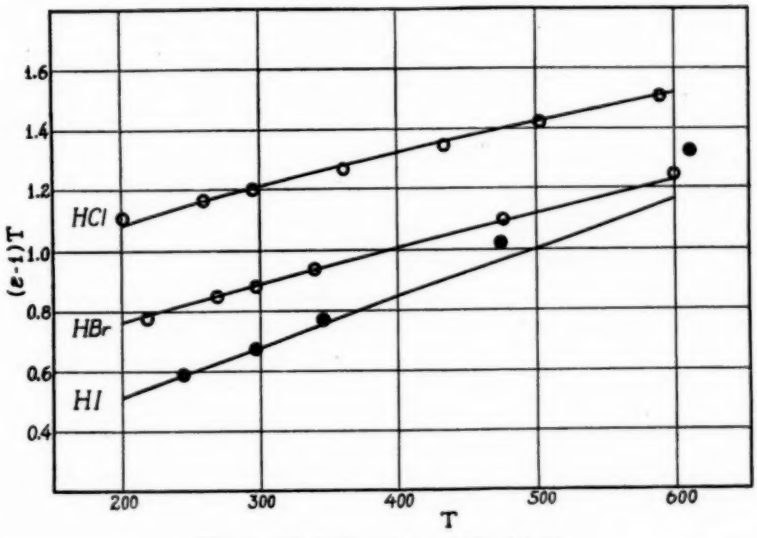

Fig. 1. Variation of $(\epsilon - 1)$T with T.

The interpretation of the data for hydrogen iodide is made difficult by the dissociation of the gas into its elements. It is desirable to obtain some information regarding the electric moment of these molecules, however, and so a different procedure has been followed. At the lowest temperature used, 244.5°A, Zahn obtained the value 0.5885 for $(\epsilon - 1)_0 T$, a value which can be accepted as correct, for the dissociation of hydrogen iodide is at that temperature only 1.3 percent. If the value 0.00160, obtained from optical data and discussed in the next section of this paper, be accepted as correct for $4\pi N_0\alpha$, then the value 0.146×10^{-18} cgsu for μ is required in order that the theoretical curve (shown in Fig. 1) might pass through this experimental point.

Discussion of Results

The electric moments of the hydrogen halides. The values found for the electric moment μ of these gases are given in Table II, together with the classical theory values given by Zahn. It is to be noticed that the classical moments are not approximately equal to those obtained from the quantum theory, but are much larger—about three times as large. In these cases, then, considerations regarding, for example, molecular structure based on the classical values of the electric moments must be revised,[8] as has already been pointed out by Pauli[3] and by Ebert.[9] Indeed, it is probable that in the case of polyatomic molecules also the classical values of the electric moments may be considerably in error.

Table II

	μ		d	
	Quantum	Classical	Quantum	Classical
HCl	0.3316×10^{-18}	1.034×10^{-18}	0.0694 A.	0.217 A.
HBr	.252	0.788	.0528	.165
HI	.146	.382	.0306	.080

Under d in Table II is given the distance between an electron and a proton in order that the configuration might have the electric moment found for each of the hydrogen halides.

Their coefficients of induced polarization. In Table III are given the values found for $4\pi N_0\alpha$ for hydrogen chloride and bromide, and those given by Zahn with the use of the classical theory. The quantum theory values are confirmed by independent evidence; for they agree with Maxwell's relation $4\pi N_0\alpha = n_0^2 - 1$, in which n_0 is the index of refraction of the gas at standard conditions for light of frequency far from any frequency characteristic of the molecule. It is known that n determined with ordinary light is larger than n_0; hence the observed values of n^2-1 for the sodium D lines, given in Table III, cannot be reconciled with the considerably larger classical theory values of $4\pi N_0\alpha$, but support the quantum theory values.

Table III

	$4\pi N_0\alpha$		n^2-1 (sodium D lines)
	Quantum	Classical	
HCl	0.00077	0.001040	0.000888
HBr	.00102	.001212	.001140
HI	(.00160)	.001856	.001812

It will be seen that the values found for $4\pi N_0\alpha$ for hydrogen chloride and bromide are in each case about 88 percent of those for n^2-1 for

[8] See, for example, Smyth, Jour. Amer. Chem. Soc. **46**, 2151 (1925); Phil. Mag. **47**, 530 (1924).

[9] Ebert, Zeits. f. Phys. Chem. **114**, 429 (1925).

the sodium D lines. For this reason it has seemed probable that $4\pi N_0\alpha$ for hydrogen iodide can be taken to be 0.00160, which is 88 percent of n^2-1 for this gas.

The discrepancies between the theoretical curve and the experimental points. The experimentally found points for hydrogen chloride and bromide cannot be made to fall exactly on a curve of the type required by the quantum theory considerations of this paper. It is possible that experimental errors are responsible for this disagreement; further experiments are accordingly desired. On the other hand, the theoretical treatment has perhaps been over-simplified. The assumption that μF is much smaller than W is valid; thus for hydrogen chloride with fields of 10,000 volts/cm μF is less than 1×10^{-17} ergs, while W for the lowest quantum state ($m=\frac{1}{2}$) is over 50×10^{-17} ergs. We have further assumed the molecule to have a definite electric moment μ, independent of its state of rotation. That this assumption also is valid has been shown in the following way. The force tending to restore the proton to its equilibrium position when it is pulled away from the chlorine nucleus can be determined from oscillation-rotation spectra.[7] Equating this with the centrifugal force acting when the molecule is in rotation, it is possible to find the change in position of the nucleus on going from one state to another. The electric moment of hydrogen chloride is only about 6 percent of that which would be caused by a single negative charge located on the chlorine nucleus and a single positive charge on the proton; it seems reasonable then that an upper limit for the change in moment occurring on moving the proton in the molecule would be given by the product of the unit charge and the distance moved. On carrying out this calculation it is found that the possible changes in the electric moment are far too small to be of any influence on the dielectric constant.

The small lack of agreement between experiment and theory accordingly remains unexplained.

The choice of quantum numbers. The pure rotation spectrum of hydrogen chloride in the far infra-red definitely requires that m be given the values 1/2, 3/2, 5/2, $\cdots\cdots\infty$.

Kratzer[10] has advanced arguments supporting the contention that half quantum numbers are only apparent, and that in the quantization of the entire dynamical system the quantum numbers assume integral values. In the hydrogen halides he supposes to be present due to the motion of electrons an angular momentum vector perpendicular to the line joining the nuclei and of magnitude $\frac{1}{2}h/2\pi$. In order for

[10] Kratzer, Ann. d. Physik, **71**, 72 (1923).

the total angular momentum to be an integral multiple of $h/2\pi$ the rotation of the molecule would have to contribute the amount $mh/2\pi$, with m having half-integral values. Kramers and Pauli[11] suggest that the electronic angular momentum vector has the magnitude $h/2\pi$ and makes an angle of 30° with the line joining the nuclei, so that its component normal to this line is $\frac{1}{2}h/2\pi$. It is evident that these theories would lead to expressions for $\overline{\overline{\cos}}\theta$ differing from that used in this paper. It has not seemed worth while to evaluate these expressions; expecially in view of the fact that hydrogen chloride is diamagnetic, for if the presence of electronic angular momentum requires the presence of a magnetic dipole the theories of Kratzer and Kramers and Pauli would require it to be paramagnetic.

If it be assumed, then, that in some cases quantum numbers can have half-integral values, there are two possibilities for n, for it can be placed equal to $0, \pm 1, \pm 2, \cdots \pm(m-\frac{1}{2})$, or to $\pm 1/2, \pm 3/2, \pm 5/2, \cdots \pm m$. It is necessary to include $n=0$ in the first group, for with $m=\frac{1}{2}$ this is the only integral value allowed. It can be shown unambiguously that the values $n=0, \pm 1, \pm 2, \cdots \pm(m-\frac{1}{2})$ cannot be correct. For with them the equation

$$C=\frac{1}{2\sigma}\,\frac{\sum_{r=1}^{\infty}\left(-\frac{1}{4(r-\frac{1}{2})^3}\right)e^{-\sigma(r-\frac{1}{2})^2}}{\sum_{r=1}^{\infty}(2r-1)e^{-\sigma(r-\frac{1}{2})^2}} \tag{23}$$

is obtained in place of Eq. (13); this equation, however, leads to negative values of C for all values of σ. Consequently Eq. (23) requires that at all temperatures the hydrogen chloride gas possess a *negative* polarization due to permanent dipoles. *The experimental measurements of the dielectric constants of the hydrogen halides accordingly rule out the quantum-number assignment*

$m=1/2, 3/2, 5/2, \cdots \infty$, $n=0, \pm 1, \pm 2, \cdots, \pm(m-\frac{1}{2})$.

The remaining assignment, with $n=\pm 1/2, \pm 3/2, \pm 5/2, \cdots, \pm m$, has then been used in this paper. It is to be emphasized that this assignment is not compatible with the idea that true quantum numbers are integral, and that half-quantum numbers result from the presence of an angular momentum vector due to the motion of electrons.

The possibility of weak quantization. The sharpness of the band spectra shows that the quantization with respect to the total quantum number m is strong; this is to be expected, for the molecule goes through

[11] Kramers and Pauli, Zeits. f. Physik, **13**, 351 (1923).

many rotations between collisions. On the other hand weak spatial quantization might occur.

If all orientations were equally probable; i. e., if there were completely weak spatial quantization, the average value of $\cos\theta$ for rotators with quantum number m would be given by Eq. (9) with n^2/m^2 replaced by the average value of $\cos^2\beta$, which is $\frac{1}{3}$; β is the angle between the axis of rotation of the molecule and the lines of force of the applied field. $\overline{\cos}\theta$ would then be zero; in other words, there would be no polarization due to permanent dipoles. This is in agreement with the result of Alexander,[12] who showed that *on the classical theory of all of the polarization is caused by molecules whose total energy is less than μF.* Since there are actually no such molecules present, polarization must arise from some other mechanism. This mechanism is spatial quantization.

We have assumed strong spatial quantization in determining the values of μ; if this assumption is incorrect, the values given are too low. But if the spatial quantization had been weak the dielectric constant would have varied with the field strengths applied. Such a variation has never been reported; Zahn and Bädeker, using different experimental methods and undoubtedly different field strengths, obtained the same values for ϵ for hydrogen chloride. It accordingly seems highly probable that there is strong spatial quantization with respect to the applied electric field.

A brief account of this work has been published in the Proceedings of the National Academy of Sciences.[13]

GATES CHEMICAL LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA.
February, 1926.

[12] Alexandrow, Phys. Zeits. **22**, 258 (1921).
[13] Pauling, Proc. Nat. Acad., **12**, 32 (1926).

THERMIONIC PHENOMENA CAUSED BY VAPORS OF RUBIDIUM AND POTASSIUM

By Thomas J. Killian*

Abstract

Thermionic effects similar to those studied by Langmuir and Kingdon for caesium have been found for rubidium and potassium. Because of the difference in the electron affinity of tungsten (4.53 volts) and that of an atom of rubidium or potassium (4.16 and 4.32 volts respectively) positive ions are formed which at filament temperatures above 1000° are drawn to the cylindrical collector from the coaxial filament. Below this temperature the ions are adsorbed on the surface of the filament and decrease its work function raising the electron emission. The degree of *thermal ionization* at various filament temperatures is found to be within the experimental error of that determined from Saha's equation. At low temperatures the filament is partially covered by adsorbed ions and the *electron emission* increases exponentially with the reciprocal of the temperature. A transition region is reached as the average life of an atom on the surface becomes shorter and then the emission decreases logarithmically with the reciprocal of the temperature. The curves and values are given. The *positive ion emission* increases logarithmically with the reciprocal of the temperature until a certain fraction of the atoms striking the filament is ionized. Further increase in temperature causes every atom to be ionized. The coincidence of experimentally determined points with the theoretical space charge curve shows each ion to have the mass of a single atom in the range of pressures studied.

Vapor pressure of rubidium and potassium.—The vapor pressure of rubidium and potassium is calculated from the maximum ion current; for rubidium $\log p = 10.55 - 4132/T$ and for potassium $\log p = 11.83 - 4964/T$; here p is in bars.

THE thermionic effects caused by caesium vapor have previously been studied by Langmuir and Kingdon.[1,2,3] This work was undertaken in order to compare the similar effects caused by the vapors of the other alkali metals.

A tungsten filament heated above 1200°K in caesium vapor was found to convert every caesium atom striking it to a caesium ion. This is due to the fact that the electron affinity of tungsten (work function) is 4.53 volts while that of caesium (ionizing potential) is only 3.88 volts. It was shown that by decreasing the work function of the filament to 2.69 volts by allowing a monatomic layer of thorium

* Graduate student of Co-operative Course in Electrical Engineering, Massachusetts Institute of Technology.

[1] I. Langmuir and K. H. Kingdon, Science **57**, 58 (1923).

[2] K. H. Kingdon and I. Langmuir, Phys. Rev. **21**, 380 (1923).

[3] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. A **107**, 61 (1925).

atoms to accumulate on the surface,[4] the positive ion emission became negligible.[3] The positive ions formed at the pure tungsten surface must be drawn to it by an image force. Below 1200°K they evaporate so slowly that the surface becomes partially covered by adsorbed caesium ions. This however lowers the electron affinity of the surface and when about 20 percent is covered the electron affinity of the surface is less than that of the atoms of caesium and no more ions are formed. However this decrease in the electron affinity greatly increases the electron emission from the surface. At a pressure of caesium corresponding to 20°C they obtained 4×10^{-5} amps. per cm² at a filament temperature of 670°K. Since the ionizing potentials of rubidium and potassium are 4.16 volts and 4.32 volts respectively it was expected that vapors of these metals would produce similar effects.

Apparatus

The tubes contained a pure tungsten filament of diameter 0.0051 cms mounted coaxially with a nickel cylinder of diameter 1.905 cms. In some tubes this collector was 2.54 cms long and in others 5.08 cms. This cylinder was between two other cylinders of the same diameter and of length 7.62 cms, the distance between them being from .08 cms to .16 cms. At each end of the filament a 6 mil tungsten spring took up the expansion due to heating. The tubes were exhausted by means of a condensation pump while being baked out at 360°C for 3 hours. The collectors were freed from gas by being heated to redness by means of induced high frequency currents. The filaments were flashed at a high temperature while the tubes were on the pump.

The smaller plate currents were measured by means of a Leeds and Northrup testing galvanometer and the larger ones by means of a microammeter. A General Electric deflection potentiometer gave the filament current. With the tube as constructed the two outer cylinders act as guard cylinders and the temperature of the part of the filament in the center cylinder is not affected more than 0.1 percent at 750°K by cooling effect of the leads. The temperature scale used is that of Forsythe and Worthing.[5]

Thermal Ionization

In the paper[3] referred to, the modified form of Saha's equation was used to determine the degree of thermal ionization. The equilibrium constant is given by

$$K_n = n_e n_p / n_a$$

[4] I. Langmuir, Phys. Rev. **22**, 357 (1923).
[5] W. E. Forsythe and A. G. Worthing, Astrophys. J. **61**, 146 (1925).

where n_e, n_p and n_a are respectively the number of electrons, of positive ions and of atoms per unit volume. For any alkali metal

$$\log_{10} K_n = 15.365 + \frac{3}{2}\log_{10} T - \frac{11{,}600\ V}{2.303\ T}$$

where V is the ionizing potential and T the absolute temperature. This expression for K_n has the dimensions of number per unit volume. Experimentally we have to do with currents and may define

$$K_I = I_e I_p / I_a$$

Where I_e and I_p are respectively the electron and positive ion emission per unit area at any filament temperature and I_a is the current density corresponding to the ionization of every atom hitting the filament. Then

$$K_I = eK_n\sqrt{\frac{kT}{2\pi m_e}} = 2.481\times10^{-14}\ K_n\ \sqrt{T} \quad \text{amp. per cm}^2$$

For rubidium

$$\log_{10} K_I = 1.7792 + 2\log_{10} T - 20{,}932/T$$

The equilibrium constants found experimentally at various filament temperatures were about one-half those calculated theoretically. That is with a filament temperature of 1302°K the equilibrium constant was found to correspond to a filament temperature of 1273°K. The logarithm of the emission was plotted against the square root of the voltage to correct for the Schottky[6] effect. At any filament temperature the slopes were found to be the same for both ions and electrons and about double that calculated from Schottky's formula. Thus it is seen that the results obtained for the equilibrium constant are probably within the experimental error furnishing further verification of Saha's assumptions.

Electron Emission

As in the case of caesium at low temperatures a tungsten filament in rubidium or potassium vapor becomes covered with a layer of adsorbed atoms. As the temperature of the filament is increased the electron emission increases logarithmically with the reciprocal of the temperature. However as the filament temperature is further increased the current reaches a maximum and then decreases as the temperature is raised due to the evaporation of the atoms at the higher temperatures.

[6] W. Schottky, Phys. Zeits. **15**, 872 (1914).

By flashing the filament in oxygen before introducing the alkali metal the filament becomes covered with a layer of oxygen atoms which is not evaporated off below 1600°K. This layer tends to hold the alkali metal on at higher temperatures and thus the emission at a given filament temperature is higher from an oxygen coated filament in the alkali metal vapor than from a pure tungsten filament.

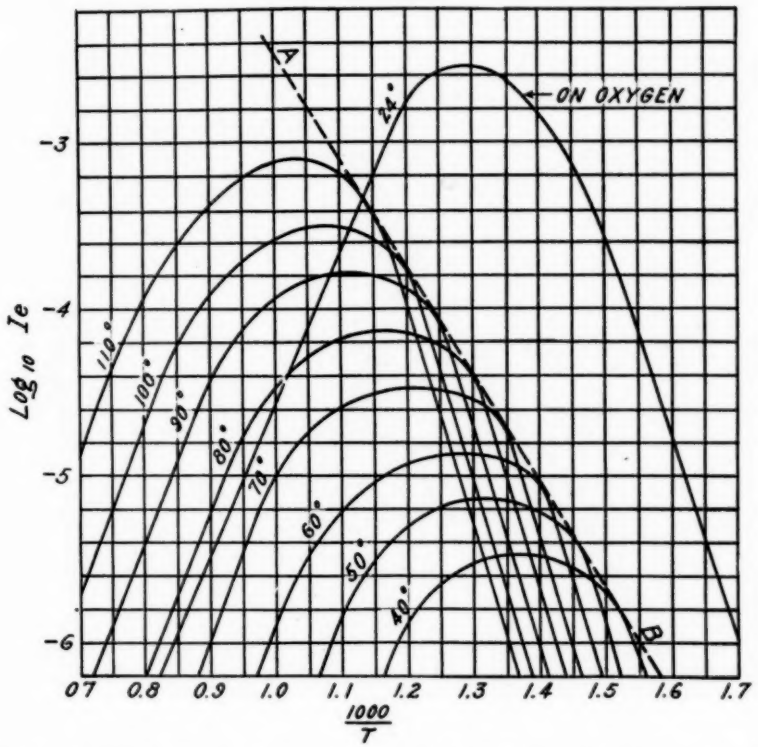

Fig. 1. Electron emission in amperes per cm² from a tungsten filament in rubidium vapor at various pressures. Temperature of bulb in °C on each curve.

Figs. 1 and 2 give the family of curves of the electron emission of filaments in the presence of rubidium and of potassium vapor. The ordinates are the common logarithms of I_e, the electron current in amp per cm², and the abscissas are the reciprocals of the absolute temperature of the filament multiplied by 1000. The temperature of the bulb which fixed the vapor pressure is given in degrees Centigrade on each curve. Before each reading the filament was flashed at a high temperature to drive off any impurities.

In the curves with the metal adsorbed on the pure tungsten surface we see that, as in the case of caesium, each curve consists of three

parts: (1) a low-temperature region where the logarithm of the emission is a straight line when plotted against the reciprocal of the temperature; (2) an intermediate region where the plot in Figs. 1 and 2 is curved; (3) a high temperature region where again the logarithm of the current is a linear function of the reciprocal of the temperature. The curves are very much alike and differ principally in being displaced parallel to their envelope A B. These displacements are proportional to the

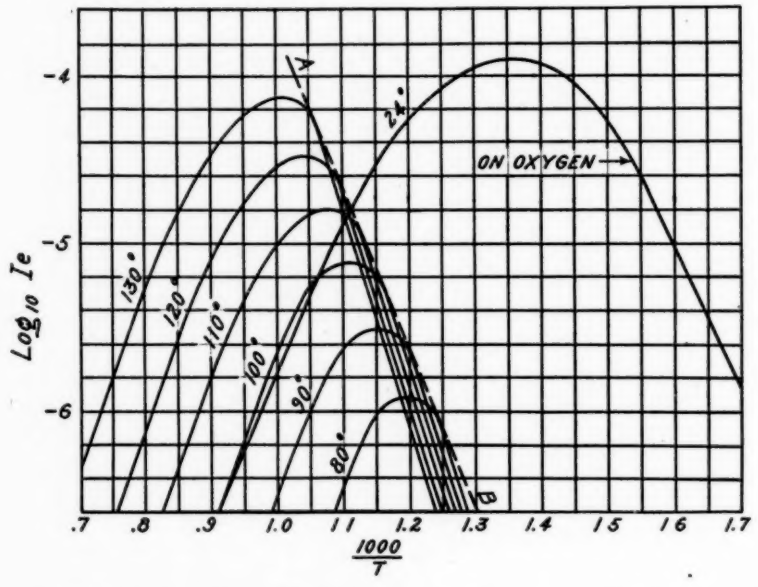

Fig. 2. Electron emission in amperes per cm² from a tungsten filament in potassium vapor at various pressures. Temperature of bulb in °C on each curve.

logarithms of the pressures of the vapor. Thus in regions (1) and (2) we may say that approximately

$$I_e = \alpha p^{\gamma} \epsilon^{-\beta/T}$$

From the curves in Figs. 1 and 2 we obtain the results shown in Table I for the constants α, β and γ.

I is in amp. per cm² and p in bars.

Positive Ion Emission

The positive ion emission at any vapor pressure increases exponentially with the reciprocal of the filament temperature until the emission is about 20 percent of the maximum when there is a definite discontinuity. Further increase in temperature causes every atom to be ionized. Thus, as in the case of caesium, there is the same evidence of

the existence of two surface phases on the filament, one in which only a fraction of the atoms is ionized and the other in which all of them are. There is a definite boundary between them and the rate at which

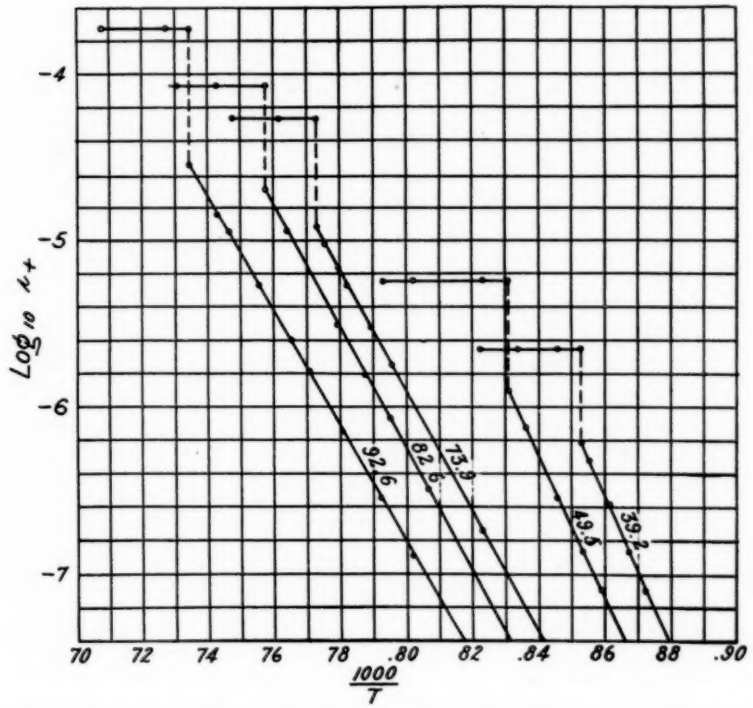

Fig. 3. Positive ion emission in amperes from a tungsten filament of area 0.0405 cm² in rubidium vapor at various pressures. Collector voltage = −200. Temperature of bulb in °C on each curve.

TABLE I

Values of the constants α,β,γ of Eq. (1).

Filament coating	α	β	γ
Rubidium on tungsten			
Region (1)	2.86×10^{12}	32,000	−1.12
Region (3)	2.08×10^{-12}	−24,000	+2.52
Rubidium on adsorbed oxygen			
Region (1)		28,000	
Region (3)		−23,000	
Potassium on tungsten			
Region (1)	5.9×10^{9}	30,800	−0.328
Region (3)	1.27×10^{-13}	−25,600	+2.66
Potassium on adsorbed oxygen			
Region (1)		19,700	
Region (3)		−23,000	

it moves along the filament can be easily measured by observing the microammeters in series with the three collectors. This velocity is found to depend upon the collector voltage and filament temperature. Langmuir and Kingdon[7] have obtained for caesium curves similar to those in Figs. 3 and 4.

If every atom is converted into a single ion a measure of the maximum positive ion current would be an accurate way of determining the vapor

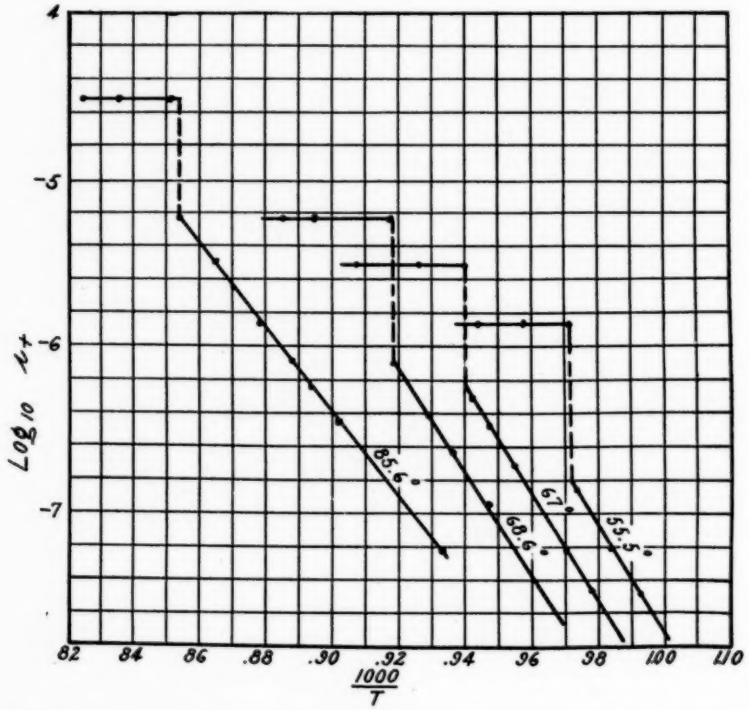

Fig. 4. Positive ion emission in amperes from a tungsten filament of area 0.081 cm² in potassium vapor at various pressures. Collector voltage = −200. Temperature of bulb in °C each on curve.

pressure. The currents limited by space charge with long coaxial cylinders is given by[8]

$$i = 14.68 \times 10^{-6} \sqrt{m_e/m_p}\ V^{3/2}/r\beta^2$$

here i is in amperes per cm length of filament, m_e and m_p the masses of an electron and positive ion respectively, V the potential of the collector below the filament in volts, r the radius of the collector and β^2 a

[7] Langmuir and Kingdon, unpublished work.
[8] Langmuir, Phys. Rev. 2, 450 (1913).

function of the ratio of the diameters of the collector and filament. In this case $\beta^2 = 1.04$.

In Figs. 5 and 6 are plotted the theoretical ion currents limited by space charge assuming the mass of a positive ion to be that of a single atom. The points were experimentally determined and corrected for

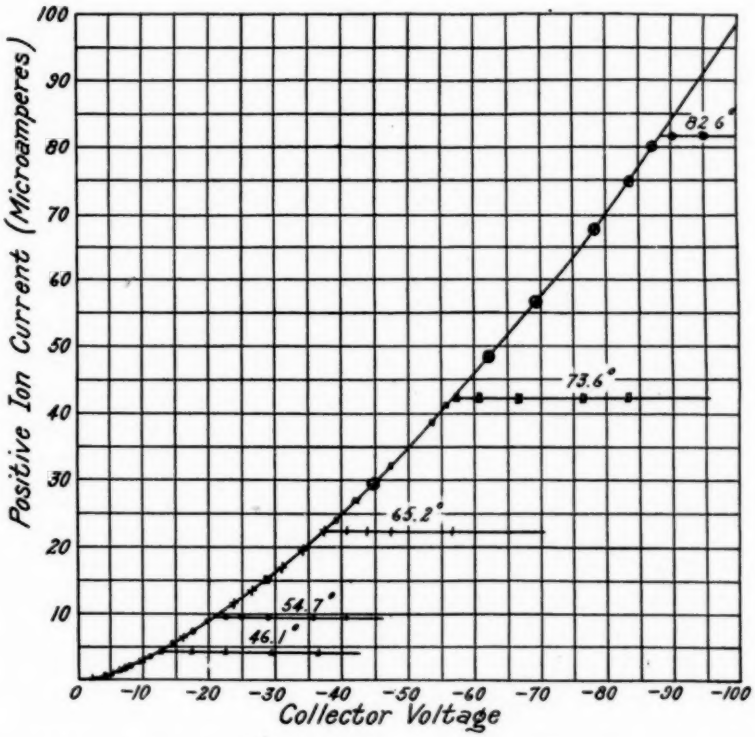

Fig. 5. Rubidium positive ion current limited by space charge at various vapor pressures. Full line is theoretical curve $I_+ = 0.0985\ V^{3/2}$. Temperature of bulb in °C on each curve.

contact potential. They check very accurately with the theoretical curve, showing that in the range of pressures studied the mass of the positive carrier is that of a single atom.[9]

Vapor Pressure

From the kinetic theory we know that the maximum positive ion current i_+ is $ep/\sqrt{2\pi mkT}$ abamperes per cm² where e is the charge on

[9] Since this work was done H. E. Ives in Jour. Frank. Inst. **201**, 62 (1926) claims this is not true at vapor pressures below those corresponding to a temperature of 60°C for caesium, rubidium and potassium.

an electron, p the pressure in bars, m the mass of an atom, k the Boltzmann constant and T the absolute temperature.
For rubidium

$$i_+ = .457\ p/\sqrt{T} \text{ amperes per cm}^2$$

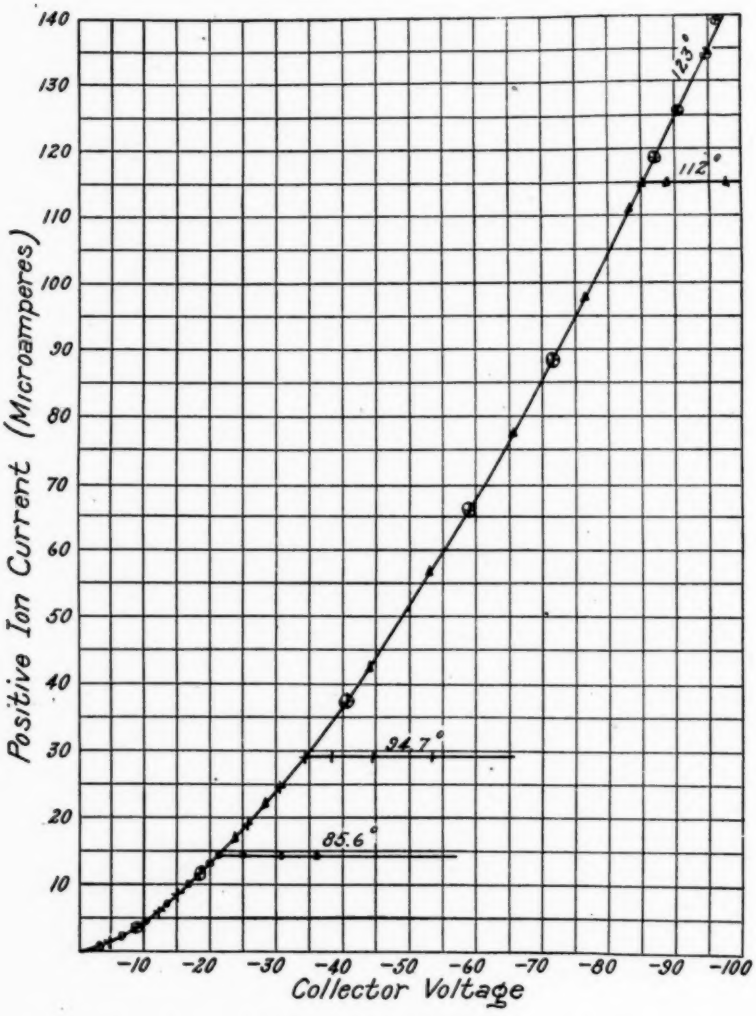

Fig. 6. Potassium positive ion current limited by space charge at various vapor pressures. Full line is theoretical curve $I_+ = 0.1452\ V^{3/2}$. Temperature of bulb in °C on each curve.

and for potassium

$$i_+ = .657\ p/\sqrt{T} \text{ amperes per cm}^2$$

Fig. 7 presents the vapor pressures of caesium, rubidium and potassium found by this method. The curve for caesium is taken from the results of Langmuir and Kingdon.[3]

For rubidium

$$\log_{10} p = 10.55 - 4132/T$$

For potassium

$$\log_{10} p = 11.83 - 4964/T$$

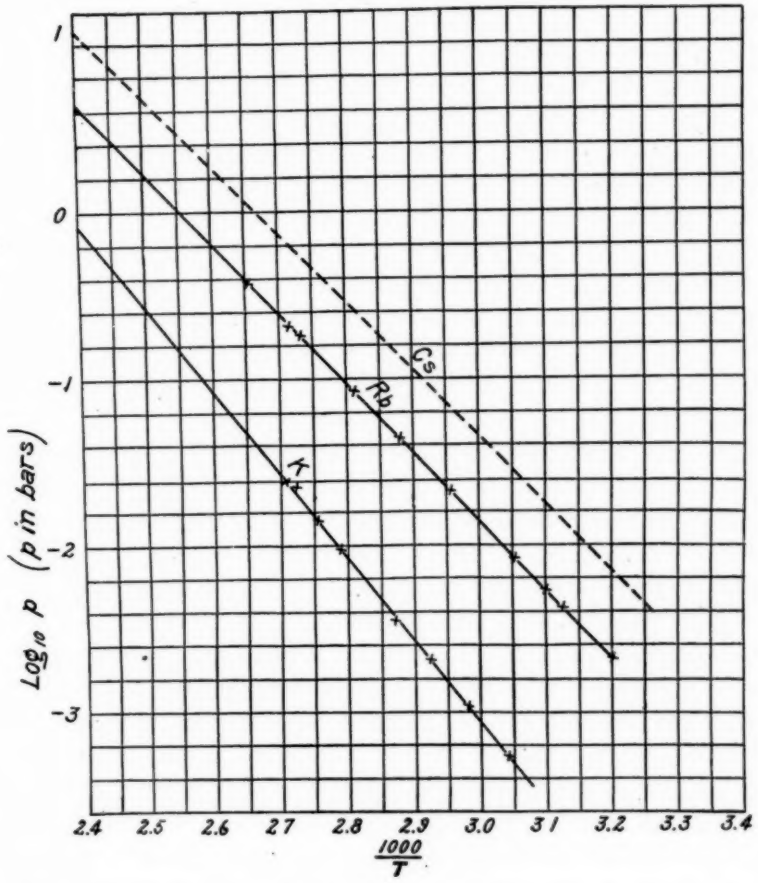

Fig. 7. Vapor pressures of Cs, Rb, and K at various temperatures as determined by the positive ion method.

I desire to express my gratitude to Dr. Irving Langmuir and Dr. K. H. Kingdon for suggesting this work and aiding me in its completion.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, NEW YORK,
February 9, 1926.

THE MOTION OF ELECTRONS IN HYDROGEN AND HELIUM

By H. B. Wahlin

Abstract

Mobilities of electrons in H_2 and He at 760 mm pressure have been measured by the Rutherford alternating potential method for fields ranging from 0.5 to 46 volts/cm. The limiting mobilities for zero field are calculated to be, for H_2, 6,700 cm/sec per volt/cm and for He, 10,840 cm/sec per volt/cm.

Energy loss of an electron on impact in H_2 and He.—*K. T. Compton's theory of electronic mobilities* is shown to fit the observed variation of mobility with field strength provided it be assumed that the fraction of its energy an electron loses on impact is, in H_2, 2.16, and in He, 8.6 times what it would be were the collisions elastic.

Mean free path of electrons in H_2 and He.—From the limiting values of the mobilities at zero field it is calculated that the mean free path of electrons in thermal equilibrium with the gas is for H_2 at 1 mm pressure, 0.0408 cm, and for He at 1 mm pressure, 0.066 cm. These values are approximately half the kinetic theory values.

THE motion of electrons through a gas under the action of an electric field has been studied by Townsend and Bailey,[1] Loeb,[2] and the writer.[3] Using a method in which the velocity in the direction of the field was determined by a magnetic deflection and in which the velocity of agitation was determined from the lateral diffusion of the electron beam, Townsend and Bailey have succeeded in showing that the velocity of drift of the electrons per unit field intensity is not independent of the field as is the case with ions, but decreases with increasing voltage. This is due to two causes. First, the electrons are not in thermal equilibrium with the gas, but, because of energy gained in the field, reach a thermal velocity which exceeds that of the gas. Secondly, as has been shown by Ramsauer[4] the electron free path is not a constant, but decreases with increasing velocity of agitation for low velocities and increases again for higher velocities.

Townsend's method is not very well adapted to a study of the motion of electrons in low fields, and for that reason it was thought best to extend the measurements on the determination of electron free paths to such small fields that the electrons may be considered to be

[1] J. S. Townsend, J. Franklin Inst. 563 (Nov. 1925).
[2] L. B. Loeb, Phys. Rev. **20**, 397 (Nov. 1922); **23**, 157 (Feb. 1924).
[3] H. B. Wahlin, Phys. Rev. **23**, 169 (Feb. 1924).
[4] C. Ramsauer, Ann. d. Physik **64**, 513 (1921); **66**, 546 (1922).

in thermal equilibrium with the molecules. A second purpose of the present investigation was to see if a comparison could be made between the experimental results and a theoretical equation for electron mobilities derived by K. T. Compton.

The method used was the Rutherford alternating potential one with a Hartley oscillating circuit as a source of alternating potential. It differed only in detail from the one described in an earlier paper dealing with electron motion in nitrogen. The alternating potential was measured by a Kelvin multicellular voltmeter from 120 to 30 volts and by an electrometer with a phosphor bronze suspension below 30 volts.

The hydrogen was purified by passing it over hot copper, through a tube containing fused calcium chloride, through a second tube containing potassium hydroxide and slowly through a system of tubes 225 cm long containing phosphorus pentoxide.

In order to purify the helium (which originally contained about 2 percent oxygen and nitrogen) three traps each containing about 170 cc of finely divided charcoal were used. The charcoal had been activated with steam and was baked at a temperature of 300°C for 24 hours or more. The third trap was so arranged that it was connected permanently to the chamber holding the gas, and the helium circulated through this continuously by convection, while the readings were being taken. No change in the results could be noticed after circulating for a period of 24 hours so that it seems reasonable to assume that the gas was pure.

All determinations were made at a pressure of 760 mm. In obtaining the mobility curves, the frequency was kept constant and the alternating potential varied. From the intercepts of the mobility curves obtained by plotting the current against field intensity, approximate values of the mobility were computed from the equation

$$u = \pi n d/\sqrt{2x} \qquad (1)$$

where n is the frequency, d the distance between the plates, and x the effective value of the alternating field.

Figs. 1 and 2 illustrate the types of curves obtained in H_2 and He respectively. It is to be noted that the intercepts are well defined so that any error arising from an ill-defined intercept was slight. In the case of curves obtained with low frequencies, i. e. where the intercept came in low fields, a number of curves were obtained without changing the frequency, and the mobility computed from the average value of the intercept thus obtained.

The mobilities computed from Eq. (1) are plotted as a function of the field intensity in Figs. 3 and 4, Fig. 3 for H_2 and Fig. 4 for He. As the mobility is not a constant, the values for higher fields must be

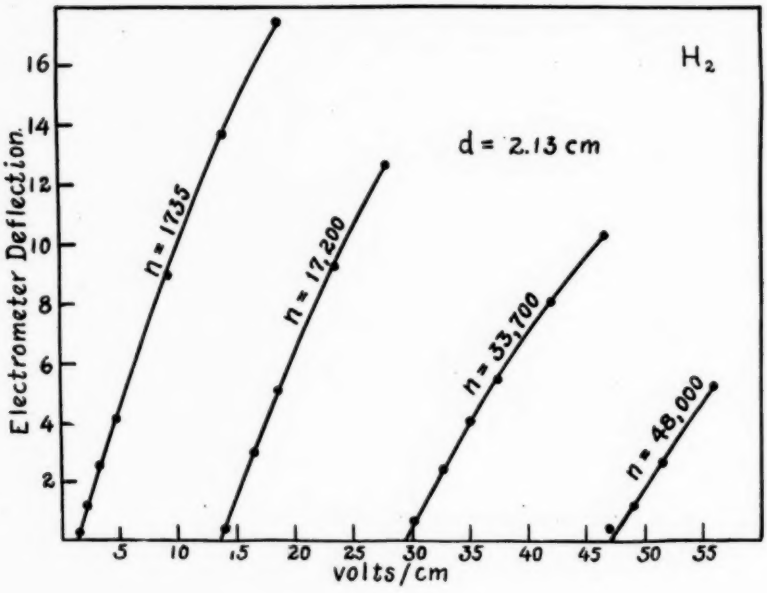

Fig. 1.

considered as approximate only, since in the derivation of Eq. (1) it is assumed that the mobility is independent of the field, and in

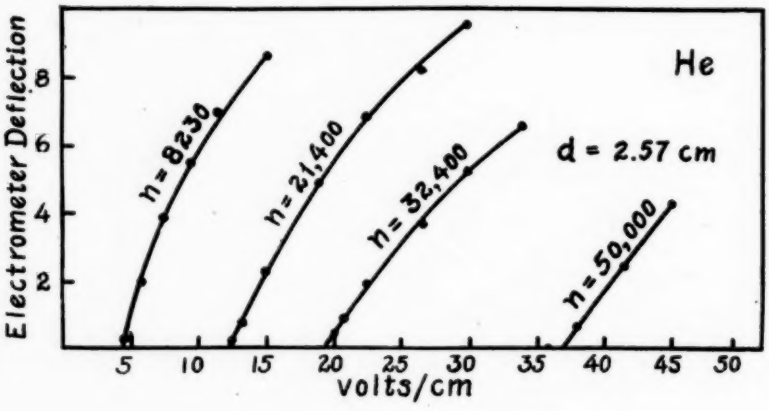

Fig. 2.

general this is far from being the case. However, an examination of these curves will show that for low fields the mobility is so nearly independent of the field that Eq. (1) is applicable and the true value of

the limiting mobility may be obtained directly from it. The values thus obtained are:

$$u_{H_2} = 6700 \text{ cm/sec per volt/cm},$$
$$u_{He} = 10{,}840 \text{ cm/sec per volt/cm}.$$

The use of the alternating potential method for determining mobilities has been criticized because the electrons do not move through the gas with the thermal velocity corresponding to the instantaneous values of the field. Compton has shown, however, that the distance the electrons must travel to gain even 99 percent of their terminal energy is small at a pressure of 760 mm, so that the error would be slight. There would be a phase lag between the terminal energy and the instantaneous value of the field driving the electrons from one plate to

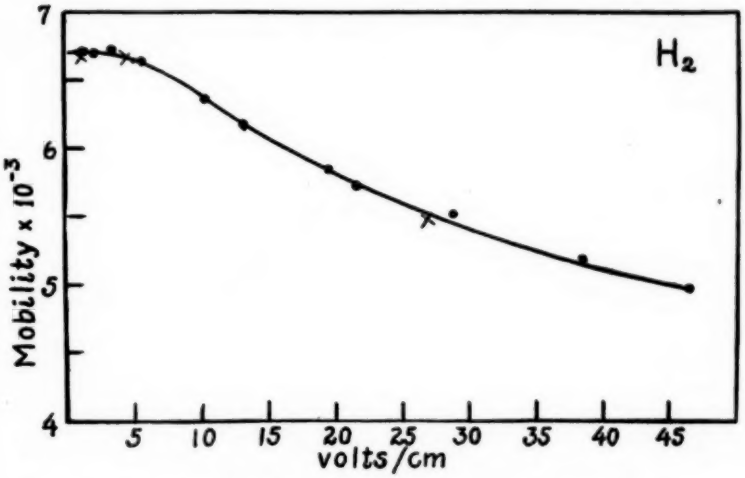

Fig. 3. Variation with field strength of electron mobilities in hydrogen.

the other. In other words, during that part of the half-cycle when the voltage is rising, the thermal energy is less than it should be, and during the part of the half-cycle when the voltage is decreasing it is greater. These two errors would tend to counterbalance each other.

In order to settle definitely any doubt concerning the question of terminal energy, the distance between the plates was varied from 2.13 cm to 4.0 cm in the case of H_2. The values represented by the dots (Fig. 3) were obtained with the former distance, and the values corresponding to the crosses with the latter. It will be noticed that they do not differ appreciably, so that any effect due to a non-terminal state is slight.

Test of Compton's Equation for Mobility

As stated above, Eq. (1) is applicable only over that range of field intensities for which the mobility may be considered as constant. When the field becomes so large that the thermal energy of the electrons differs appreciably from the molecular, the mobility will decrease because of the decreased time between impacts. In general, then, the mobility will be a function of the field. K. T. Compton[5] has derived this function and has shown that

$$u=\frac{.815\, e\lambda}{\sqrt{m}\left[\alpha T+(\alpha^2T^2+1.76\lambda^2e^2x^2/f)^{\frac{1}{2}}\right]^{\frac{1}{2}}}$$

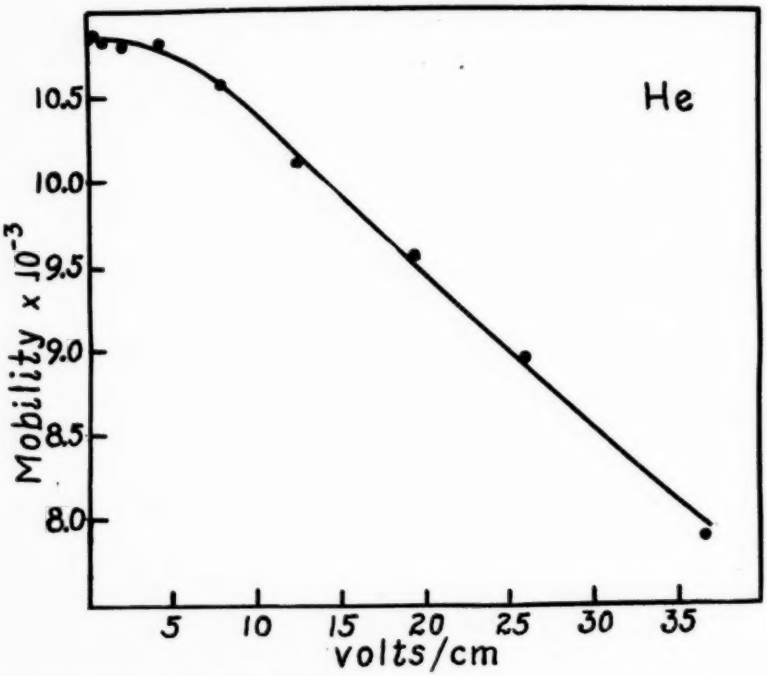

Fig. 4. Variation with field strength of electron mobilities in helium.

where e is the electronic charge, λ the mean free path, αT the thermal energy of the molecules, and f the fraction of its energy an electron loses on impact with a molecule.

This equation may be written in the form

$$u=\frac{a}{\left[1+(1+Bx^2)^{\frac{1}{2}}\right]^{\frac{1}{2}}}$$

if it is assumed that λ is independent of x.

[5] K. T. Compton, Phys. Rev. **22**, 333 (1923).

The equation of motion of the electrons would then be

$$\frac{dy}{dt} = \frac{ax}{[1+(1+Bx^2)^{\frac{1}{2}}]^{\frac{1}{2}}}$$

where x is the instantaneous value of the field, and dy/dt is the velocity in the direction of the field.

In the case under discussion since a sine field was employed, we get

$$\frac{dy}{dt} = \frac{aX \sin 2\pi nt}{[1+(1+BX^2 \sin^2 2\pi nt)^{\frac{1}{2}}]^{\frac{1}{2}}} \tag{2}$$

Thus a direct check of Compton's equation is impossible in this case. However, it is possible to compare the experimentally determined frequency necessary to obtain an intercept with a given field with those obtained by a solution of this differential equation. Eq. (2) becomes for this case

$$\int_0^d dy = \int_0^{1/2n} \frac{aX \sin 2\pi nt \, dt}{[1+(1+BX^2 \sin^2 2\pi nt)^{\frac{1}{2}}]^{\frac{1}{2}}}$$

Placing $2\pi nt = \theta$ and solving for n we get

$$n = \frac{aX}{\pi d} \int_0^{\pi/2} \frac{\sin\theta \, d\theta}{[1+(1+BX^2 \sin^2\theta)^{\frac{1}{2}}]^{\frac{1}{2}}}$$

This is an elliptic integral and on reduction gives

$$n = \frac{a\sqrt{2r}}{\pi d\sqrt{B}} [2E(k,\varphi) - F(k,\varphi)] \tag{3}$$

in which

$$r = \sqrt{BX^2+1}, \qquad k = \sqrt{\frac{r+1}{2r}} \text{ and } \varphi = \sin^{-1}\sqrt{\frac{r-1}{r+1}}$$

The values of a may be determined immediately from the limiting mobility as the field approaches zero, since in this case Compton's equation reduces to the form $u = a/\sqrt{2}$. We thus get

$$a_{\mathrm{H}} = 9{,}490 \text{ cm/sec per volt/cm}$$
$$a_{\mathrm{He}} = 15{,}350 \text{ cm/sec per volt/cm.}$$

The values of B which fit the experimental results most closely are

$$B_{\mathrm{H_2}} = .003$$
$$B_{\mathrm{He}} = .004$$

Tables I and II give the frequencies computed from Eq. (3), together with those experimentally determined.

TABLE I

Hydrogen

$a=9490$, Effective value of field	$B=.003$, n (calc.)	$d=2.13$ cm n (obs.)
1.23	1730	1735
2.09	2960	2959
3.52	4955	5000
5.73	8000	7990
10.40	14,000	14,000
13.2	17,400	17,200
19.5	24,300	24,000
21.7	26,600	26,200
28.9	33,300	33,700
38.5	41,200	42,200
46.0	46,700	48,000

TABLE II

Helium

$a=15,350$, Effective value of field	$B=.004$, n (calc.)	$d=2.57$ cm n (obs.)
.554	1055	1061
1.107	2120	2090
2.18	4160	4110
4.33	8220	8230
7.94	14,770	14,720
12.40	22,100	21,400
19.28	32,200	32,400
26.00	40,600	40,750
36.65	52,300	50,000

The agreement between the experimental and calculated values is quite close. For the higher frequency there is a slight variation which may be due to experimental errors.

CALCULATION OF MEAN FREE PATH

Since Compton's equation satisfied the experimental data so closely it must be concluded that over the range of voltages used in these experiments the mean free path is a constant and independent of the electron velocity. This is not the case in nitrogen, as shown in the article referred to above. The values for the mean free path may most readily be computed from the limiting mobility, using Townsend's equation, viz.

$$u=.75e\lambda/m\bar{v}$$

The values thus calculated for a pressure of 1 mm placing $\bar{v}=1.065\times10^7$ cm/sec. at 20°C, together with the kinetic theory values ($4\sqrt{2}$ times the molecular free path) are

	Experimental λ	Kinetic theory λ
H_2	.04080 cm	.0842 cm
He	.0660	.1313

The experimental values are thus seen to be lower than the kinetic theory values. This, however, is not in general the case. Since the experimental value of λ found for N_2 is .0996 cm at 1 mm pressure whereas according to kinetic theory reasoning it should be lower than both λ_{H_2} and λ_{He}.

Energy Loss of an Electron on Impact

In the discussion of Compton's equation above, we used it in the general form, simply assuming that the energy loss on impact is a fraction f of the electronic energy. From the experimentally determined value of B it is possible to calculate this fraction f. Since

$$B = 1.76\lambda^2 e^2 / f\alpha^2 T^2$$

we get, remembering that x is measured in volts,

$$f_{H_2} = 1.17 \times 10^{-3}$$

$$f_{He} = 2.32 \times 10^{-3}$$

If the impacts are elastic Compton has shown that

$$f = 2m/M$$

where m is the electronic and M the molecular mass. From this we get

$$f_{H_2} = .541 \times 10^{-3}$$

$$f_{He} = .270 \times 10^{-3}$$

The observed fraction is about 2.16 times what it should be on the basis of elastic impacts in H_2 and 8.6 times too large for He. The fraction lost is very small in either case and is independent of the energy of the electron at impact over the range of energies covered in these experiments. The fact that f for He is greater than that for H_2 may be due to the presence of some impurity not readily absorbed by the charcoal although it is difficult to imagine what it could be. No electronegative impurities were present, as shown by the high value obtained for the limiting mobility, and it seems reasonable therefore to conclude that other impurities were present in very small quantities.

Fortunately the mobility is independent of x and therefore also of f in low fields, so that the effect on the limiting mobility would be negligible, unless the molecular dimensions of the impurity differ enormously from those of helium.

University of Wisconsin,
Madison, Wisconsin,
January 25, 1926.

VISIBILITY PHENOMENA WITH INTERFERENCE BY MULTIPLE REFLECTIONS

By Lachlan Gilchrist

Abstract

Visibility of interference fringes due to multiple reflections of approximately monochromatic light.—Approximate expressions are developed for the intensity and visibility of interference fringes for both transmitted and reflected light when any number of multiple reflections exist and the source of light is one of small width. Where the number of reflections is large, the visibility is $V=2b^2C/P$ and $V=(1-b^2)C/P$ respectively, C and P depending on the distribution of intensity in the source and having the significance which was given them by Michelson and Rayleigh b is the coefficient of reflection at the first reflecting surface. The effects of the coefficients of reflection and absorption are examined and it is indicated that the method of visibility with interferometers which depend on multiple reflection may be used to advantage in the study of the fine structure of such spectra as those of hydrogen and helium, not only in order to obtain the components but also to determine the character of each component. It is also indicated that the development may be extended to x-ray spectra in which series of multiple reflections from numerous planes exist.

THE growing necessity of obtaining high resolution of the components of a source of radiation makes it desirable that the method of visibility of interference fringes developed by A. A. Michelson should be investigated for the case where the interference is obtained under the conditions of multiple reflections. Resolution of a very high order may be obtained and components very close in wave-length are revealed by this method, but it has the further distinct advantage that it gives the distribution of intensity in the radiation of various wave-lengths emitted by components of the source. Moreover recent developments in the quantum theory make it desirable to obtain this information of the fine structure, particularly of hydrogen and helium spectra.

Interference of homogeneous radiation of wave-number m as ordinarily obtained is represented by

$$I=2A^2(1+\cos 4\pi Dm). \tag{1}$$

For a source of small "width" this becomes

$$I=2\int_{-x}^{x} F(x)\{1+\cos 4\pi D(\bar{m}+x)\}\,dx. \tag{2}$$

If visibility is defined by the expression

$$V=\frac{I_{max}-I_{min}}{I_{max}+I_{min}} \tag{3}$$

and if the distribution of intensity in the source follows the probability law,

$$V=C/P=\frac{\int_{-\infty}^{+\infty}\exp\left[-h^2x^2\right]\cos 4\pi Dx\,dx}{\int_{-\infty}^{+\infty}\exp\left[-h^2x^2\right]dx}=\exp\left[-(2D)^2\pi^2/h^2\right] \tag{4}$$

Where there are several components in the source the visibility is expressed by

$$U^2=\frac{\sum r^2+2\sum rr'\cos 4\pi D(d'-d)}{(\sum r)^2}V^2 \tag{5}$$

If the width of the source be considered as due to a Doppler effect in which Maxwell's law of distribution of velocities exists it was shown by the late Lord Rayleigh that

$$V=\exp\left[-\pi(\pi\Delta v/\lambda c)^2\right] \tag{6}$$

and (4) has been expressed in terms of a defined width $\bar{a}$ by Michelson thus

$$V=\exp\left[-(2D)^2\pi^2\bar{a}^2/4\log 2\right] \tag{7}$$

From (6), Δ corresponding to a definite value of V was obtained and used in (7) for the same value of V, viz. one-half the maximum V. This gave for the width

$$W=(v\lambda/c)\left(2\sqrt{\pi\log 2}\right) \tag{8}$$

or where the freedom of the source is modified by density

$$W=(v\lambda/c)\left(2\sqrt{\pi\log 2}+\lambda/\rho\right) \tag{9}$$

where ρ is the mean free path of the source which was assumed to be atomic in character.

If the source is atomic in character and depends on the atomic weight and the temperature, then (9) may be expressed

$$W=\frac{\lambda}{\sqrt{m}}\frac{v_0}{c}\sqrt{\frac{T}{T_0}}\left(2\sqrt{\pi\log 2}+\lambda/\rho\right) \tag{10}$$

In the application of these formulas Michelson made use of a comparator to compare the visibility for any path difference with the maximum visibility which he defined as unity.

Now the development of instruments for investigation in which multiple reflections exist and the use of methods of getting absolute measurement of visibility make it desirable that all these formulas should be reconsidered. Further since x-ray spectra are in general formed from numerous series of multiple reflections from a large number of parallel planes it is important that visibility expressions should also be obtained for transmitted and reflected x-radiation. The Lummer and Gehrcke and the Fabry and Perot interferometers are typical instruments where multiple reflections exist and will serve the purpose of illustration. These instruments may have their reflecting surfaces silvered or clear.

The following notation will be used: I_0 is the intensity of the incident light; $\partial = 4\pi D/\lambda$ where $2D$ is the path difference between two successive rays and λ is the wave-length; p is the number of reflections; b and e are the reflection coefficients and c and f are the transmission coefficients at the two reflecting surfaces, respectively.

The expressions for the intensity are as follows:

1. For silvered plates; (a) with transmitted light

$$I = I_0 \frac{(1-b^{2p})^2 + 4b^{2p} \sin^2 (p\partial/2) c^2 f^2}{1 - 2b^2 \cos \partial + b^4} \tag{11}$$

which becomes simplified, when p is large to

$$I = I_0 \frac{c^2 f^2}{1 - 2b^2 \cos \partial + b^4} \tag{12}$$

(b) with reflected light and p large

$$I = I_0 \left[b^2 + \frac{2bcfe(\cos \partial - e^2) + c^2 f^2 e^2}{1 - 2e^2 \cos \partial + e^4} \right] \tag{13}$$

2. For unsilvered plates where the principle of reversibility may be assumed to hold if the angle of incidence is suitable and consequently $b = -e$ and $1 - b^2 = cf$;

(a) with transmitted light

$$I = I_0 \frac{(1-b^2)^2 [(1-b^{2p})^2 + 4b^{2p} \sin^2 (p\partial/2)]}{1 - 2b^2 \cos \partial + b^4} \tag{14}$$

(b) with reflected light

$$I = I_0 - \text{expression (14)} \tag{15}$$

these also may become simplified obviously if p is large. Eq. (12) may be taken as the result applicable to the Fabry and Perot interferometer if a monochromatic source emitting radiation of wave-length λ is used. Eqs. (14) and (15) represent the result obtained for the Lummer and Gehrcke plate where $\partial = \mu 4\pi D/\lambda$ in which μ is the index of refraction of the plate.

As in the case of the simple interferometer, if the source is complex (12) becomes

$$I = \int_{-x}^{x} F(x) \frac{c^2 f^2}{1 - 2b^2 \cos \partial + b^4} dx \tag{16}$$

where $\partial = 4\pi D(\bar{m} + x)$, and may be written in the form

$$I = I_0 \frac{c^2 f^2}{1 - b^4} \int_{-x}^{x} F(x)(1 + 2b^2 \cos \partial + 2b^4 \cos 2\partial + \cdots) dx \tag{17}$$

In the same way (12) may be written

$$I = I_0 \frac{c^2 f^2}{1 - b^4} (1 + 2b^2 \cos \partial + 2b^4 \cos 2\partial + \cdots) \tag{18}$$

and if $2b^4 \cos 2\partial + 2b^6 \cos 3\partial + \cdots$ may be neglected, then in (18)

$$I \doteqdot I_0 \frac{c^2 f^2}{1 - b^4} (1 + 2b^2 \cos \partial) \tag{19}$$

and in (17)

$$I \doteqdot \int_{-x}^{x} \frac{c^2 f^2}{1 - b^4} F(x)(1 + 2b^2 \cos \partial) dx \tag{20}$$

and maximum and minimum intensities are given by

$$I = \frac{c^2 f^2}{1 - b^4} (P \pm 2b^2 \sqrt{C^2 + S^2})$$

where $P = \int F(x) dx$, $C = \int F(x) \cos 4\pi Dx \, dx$, and $S = \int F(x) \sin 4\pi Dx \, dx$ and since $S = 0$ for a symmetrical source

$$I_{max} = \frac{c^2 f^2}{1 - b^4} (P + 2b^2 C) \text{ and } I_{min} = \frac{c^2 f^2}{1 - b^4} (P - 2b^2 C)$$

and therefore

$$V = 2b^2C/P = 2b^2 \exp\left[-(2D)^2\pi^2/h^2\right]. \tag{21}$$

Using Michelson's form of expression

$$V = 2b^2 \exp\left[-(2D)^2\pi^2\bar{a}^2/4 \log 2\right] \tag{22}$$

and Rayleigh's form of expression

$$V = 2b^2 \exp\left[-\pi(\pi\Delta v/\lambda c)^2\right] \tag{23}$$

an expression which was obtained by Saha[1] and by A. J. Dempster[2] by somewhat different developments.

It may be observed that by increasing b^2 a large path difference Δ may be used and the visibility will persist, for from (23)

$$\Delta = \frac{\lambda c}{\pi v}\sqrt{\frac{1}{\pi}\log\left(2b^2/V\right)} \tag{24}$$

High values of b^2 may be obtained by the use of reflection at air-metal surfaces, e. g. by silvering the plates in the Fabry and Perot and Lummer and Gehrcke interferometers. Since, however, if b^2 is high, absorption is correspondingly great, the transmitted light may be so weak as to preclude the observation of fringes unless the source is made correspondingly bright. Now however, as b^2 becomes large it is necessary to determine if the approximate formula (19) may be used for (18) and obtain a measure of the error introduced thereby.

Examples may be taken showing the magnitude of the error in the expression for the intensity introduced by the use of $(1+2b^2\cos\partial)$ for $(1-b^4)/(1-2b^2\cos\partial+b^4)$. If $b^2=0.8$ and ∂ be given values successively such that $\cos\partial = 1,\ 1/2b^2,\ 0.5,\ 0,\ -0.5,\ -1/2b^2$, it will be seen that there are errors of excess and deficiency that are of very considerable magnitude indeed.

The maxima of the fractional excess and deficiency errors may be shown to occur when $\cos\partial = 1$ or $\cos\partial = b^2/4$. In the first case the error is

$$I_0\frac{c^2f^2}{1-b^4}\left(\frac{2b^4}{1-b^2}\right)$$

and the fractional error is $2b^4/(1-b^2)$. If $b^2=0.8$ the fractional error is 0.71. In a similar manner it may be shown that if $\cos\partial = b^2/4$ the fractional error, when $b^2=0.8$, is 3.8.

The error in the expression for the intensity will be zero if $\cos\partial = (b^2 \pm \sqrt{b^4+8})/4$ unless at the same time $\cos\partial = (1+b^4)/2b^2$, in which

[1] Saha, Phys. Rev. **10**, 782 (1917)
[2] Dempster, Ann. d. Physik, **47**, 791 (1915).

case $b^2=1$. But b^2 is always less than 1 so that it is possible to find a value for ∂ for which the use of the approximate formulas under consideration is justified.

The error introduced in the expression for the visibility by the substitution of (20) for (17) may also be determined. If (19) be used for intensity the expression for visibility is given by Eq. (21). If (17) is used, then

$$I=\frac{c^2f^2}{1-b^4}(P+2b^2C\cos\theta+2b^4C_1\cos 2\theta+2b^6C_2\cos 3\theta+\cdots)$$

where P and C have the same significance as before, $\theta=4\pi Dm$, and

$$C_1=\int_{-x}^{x}F(x)\cos 8\pi Dx\,dx\ ,\quad \text{etc.}$$

Maxima exist where $\theta=2\pi$, 4π, etc., and minima where $\theta=\pi$, 3π, etc. The visibility is therefore given by

$$V=\frac{I_{max}-I_{min}}{I_{max}+I_{min}}=\frac{2b^2C+2b^6C_2+2b^{10}C_4+\cdots}{P+2b^4C_1+2b^8C_3+\cdots}\doteqdot\frac{2b^2C}{P(1+2b^4C_1/P)}$$

and if it is assumed that $F(x)$ is $\exp[-h^2x^2]$

$$V=\frac{2b^2C}{P\left(1+2b^4\exp\left[-(4\pi D/h)^2\right]\right)} \tag{25}$$

Now for low values of $2D$, $\exp[-(4\pi D/h)^2]\doteqdot 1$. It is therefore only when b^2 is a small fraction that (21) may be used to represent visibility in spectra of low order. If one obtains the ratio of the visibilities for two values of $2D$, as was done by Michelson, using, however, values of some magnitude well separated but well towards the limit of visibility, the error which is introduced by the use of (21) for (25) is greatly reduced. It is therefore evident that in the use of formula (21) for visibility and the formulas (22), (23) and (24) which are derived from (21) if the value of V is obtained by means of a silvered Fabry and Perot interferometer or any multiple reflecting instrument where the coefficient of reflection of the intensity is high that errors of some magnitude will appear in the results unless measurements are made where suitable path differences exist.

It should be observed also that the expressions for I_{max} and I_{min} were obtained by neglecting varitions of I with C and S. These were in general negligible for very narrow sources even for small differences

in path. But for large differences in path they become quite important. However where visibility is measured near the limit, i. e. for very high values of $2D$, the variations in intensity will have both deficiency and excess values depending on $\cos 4\pi Dx$ and $\sin 4\pi Dx$ and the resultant integrated variation of I with C and S will be negligible.

From (6) and (24) it is clear that the path difference for any assigned value of the visibility is $\sqrt{1-\log 2b^2/\log V}$ times that for the same value of the visibility where multiple reflections do not exist. An increase or decrease exists according as b^2 is greater or lesser than .5. Further if .025 be taken as the limiting value of V the path difference corresponding to this value may be shown from (24) to be of the order of 4 cms. Path differences for the limiting visibility much larger than this are observable experimentally. In fact Fabry[3] obtained visible fringes for a path difference of 43 cm. and Lummer and Gehrcke are credited by H. A. Lorentz[4] with using path differences of over one meter. In these cases the sources which were used emitted intensely bright light.

In the interferometers of Fabry and Perot if the surfaces are not silvered and the light is incident normally $b^2 \doteqdot 0.05$ i. e. comparatively low. The maximal excess and deficiency errors in the use of the approximate expression for intensity are negligibly small and $V = 2b^2C/P$ represents the visibility fairly well even for small path differences. In the interferometer of Lummer and Gehrcke the angle of incidence is very great and b^2 is very high even if the plate is unsilvered. If $i = 85°$ $b^2 > 0.6$ and becomes larger rapidly as the angle of incidence increases and the errors which are associated with the intensity formula are of considerable magnitude. For a fairly thick plate the path difference is large and the expression for visibility is sufficiently accurate. Since, however, only a few orders of spectral fringes appear, it may be necessary to use two plates of the same glass but of different thicknesses in order to get the ratio of the visibilities for two suitable values of the path difference.

If interference is obtained by reflected light and $c^2f^2 = (1-b^2)$ the expression for the intensity

$$I = I_0\left[1 - \frac{(1-b^2)^2}{1-2b^2\cos\vartheta + b^4}\right] = I_0\left[\frac{2b^2(1-\cos\vartheta)}{1-2b^2\cos\vartheta + b^4}\right]$$

[3] Fabry, Comptes Rendus **128**, 1223 (1899).
[4] H. A. Lorentz, Phys. Zeits. **11**, 349 (1910).

Therefore

$$I=I_0\left[\frac{2b^2}{1-b^4}(1-\cos\partial)(1+2b^2\cos\partial+2b^4\cos 2\partial+++)\right]$$

and proceeding as in the case for transmitted light, $V=(1-b^2)C/P$.

The intensity formula for use with the Lummer and Gehrcke plate for transmitted light is more accurately that given in (14) which may be written

$$I=I_0\frac{(1-b^2)^2}{1-b^4}\left[(1-2b^{2p}\cos\partial+b^{4p})(1+2b^2\cos\partial+2b^4\cos 2\partial+)\right]$$

If the source has "width" the expression for visibility reduces to (21) if b is small and p is large. Similarly for reflected light

$$I=I_0\left[1-\frac{(1-b^2)^2}{1-b^4}\{(1-2b^{2p}\cos\partial+b^{4p})(1+2b^2\cos\partial +2b^4\cos 2\partial+++)\}\right]$$

and if b is small and p is large $V=(1-b^2)C/P$.

In the development of formulas (21) and (24) no account was taken of absorption between the planes of reflection or of loss by diffuse reflection or scattering. These factors may be ignored if the interferometers are used for the measurement of wave-lengths or for the direct observation of resolved spectral components. If, however, the visibility method is to be employed to determine the character of the source these should be taken into account. If a is the coefficient or loss of amplitude due to these causes the visibility formula (21) becomes

$$V=2b^2(1-a)^2C/P$$

With this modification of (21) formula (24) would become

$$v=\frac{\lambda c}{\pi\Delta}\sqrt{\frac{1}{\pi m}\log\frac{2b^2(1-a)^2}{V}} \qquad (26)$$

if the atomic mass of the source is taken into consideration. Here a is the coefficient of loss of amplitude of the light for one passage of the light through the interferometer plate. Since the length of this path is given by $l=d/\cos\psi$ where d is the thickness of the plate and ψ is the angle of refraction or $l=\mu d/\sqrt{\mu^2-\sin^2 i}$ where μ is the index of refraction of the plate, it is seen that a varies with the angle of incidence. In the case of glass the values of both a and b are accurately known. From (26) the relationship between v and m may be obtained

even for close components of spectral lines, since these components may first be obtained by the use of auxiliary spectroscopes of high resolving power.

If the definition of visibility chosen by the late Lord Rayleigh be used in connection with multiple reflection interferometers, viz., $V=I_{min}/I_{max}$ then the considerations of errors which are introduced by the use of the approximate formula above are still applicable. With this definition

$$V=(P-2b^2C)/(P+2b^2C)$$
$$=\frac{1-2b^2\exp\left[-(2D)^2\pi^2\tilde{a}^2/4\log 2\right]}{1+2b^2\exp\left[-(2D)^2\pi^2\tilde{a}^2/4\log 2\right]}$$

replaces (16) for transmitted light.
Or in terms of the velocity of the source

$$V=\frac{1-2b^2\exp\left[-\pi(\pi\Delta v/\lambda c)^2\right]}{1+2b^2\exp\left[-\pi(\pi\Delta v/\lambda c)^2\right]}$$

or where absorption is taken into account

$$V=\frac{1-2b^2(1-a)^2\exp\left[-\pi(\pi\Delta v/\lambda c)^2\right]}{1+2b^2(1-a)^2\exp\left[-\pi(\pi\Delta v/\lambda c)^2\right]}$$

which replaces (17).

The Lummer and Gehrcke plate offers some advantages for use with this method of analysis of a source of light.

(1) The angle of incidence is perfectly definite and the coefficients of reflection of intensity of light for air-glass surface at all angles of incidence are shown to a high degree of accuracy.

(2) The group of fringes obtained is for large differences of path and by choice of plates of suitable thickness groups of fringes with well graded visibility may be obtained and measurements may be made at many points suitable for obtaining an accurate visibility curve from which to deduce the conditions in the source.

(3) The plate may be crossed with another plate, with an echelon, or with other spectroscopes and visibility curves for the resolved components thereby obtained. Where components are not resolved they will make themselves evident by a periodic condition in the visibility curve for the fringes of the resolved components.

(4) To obtain measurements of the visibility experimentally fairly accurate results may be obtained from a photograph of the fringes if a uniform beam of light is sent through the photographic plate and the intensity measured for an unaffected part of the plate as well as for the various parts of the plate on which the fringes show. This may be

sufficiently accurate since it is the $\sqrt{\log(1/V)}$ which appears in the formulas (24) and (26). However, a greater degree of accuracy will probably be obtained by the use of a thermocouple, a photoelectric cell or a selenium or thalofide cell to measure the intensities at the maxima and minima.

(5) The existence of wide minima and narrow maxima of the transmitted light presents an opportunity of obtaining greater accuracy in the measurement of visibility than is the case with the simple interferometer since owing to the width of the minima they are not difficult to locate. Moreover, since I_{max} and I_{min} are small quantities, especially for large differences in path, it is imperative that the minima should be located very accurately if the measurement of I_{min} is to be at all accurate.

For a homogeneous source like that which gives the cadmium red line the visibility curve is simple and is obtainable with accuracy by the Michelson interferometer and may be readily interpreted.

For sources of more complex structure, e. g. those of hygroden and helium spectra, it is desirable not only to resolve the fine components but also to obtain the distribution of intensity in these components. Moreover it is now highly desirable to study the Zeeman and Stark effects not only in the production of components but also on the distribution of intensity in the components for use in the elucidation of spectral series and also for the determination of the character of the source. In this work multiple reflection interferometers should be of considerable assistance.

In the spectra of x-rays which are obtained from analyzing crystals of simple form only the first four or five orders are obtainable. Since, however, both the coefficients of absorption a and of reflection b are of very small magnitude, it is possible to develop expressions for intensity and visibility which may be reasonably accurate in these low orders and which may serve to compare crystal formations and perhaps give some information on the character of the source. In this connection there has been a very extensive consideration of the intensity of radiation from imperfect crystals by C. G. Darwin[5] and expressions for the intensity of the maxima for ideally monochromatic radiation when simple and almost perfect crystals are used have been obtained by K. W. Lamson.[6]

TORONTO,
August 5, 1925.

[5] C. G. Darwin, Phil. Mag. **43**, 800 (1922).
[6] K. W. Lawson, Phys. Rev. **17**, 624 (May, 1921).

THE RADIATION OF ENERGY AND ANGULAR MOMENTUM

By H. Bateman

Abstract

When an electromagnetic field, derived from retarded potentials, is given it is generally possible to add to this a scalar field, derived from a retarded potential ψ, in such a way that the total radiation of energy to infinity is zero for each direction, the contribution of the scalar field being calculated with the aid of a tensor used in a former paper. The radiation of angular momentum to infinity is not zero for each direction unless the electromagnetic field is of a certain type. The approximate values of the field vectors at a great distance from the origin can be expressed in terms of a quantity α and when the field is of the type just mentioned α satisfies a certain partial differential equation. This result may be regarded as typical for attempts to solve the radiation problem in which the electromagnetic radiation in one of Bohr's stationary states is supposed to be balanced by radiation of a new type. Some remarks are made on the attempts which have been made to solve the problem with the aid of electromagnetic fields alone and a brief discussion is given of the radiation of angular momentum according to the classical theory.

Introduction

1. In a former paper[1] an attempt was made to justify the hypothesis of non-radiating electronic orbits by a modification of electromagnetic theory in which a scalar field, specified by a retarded potential ψ, is supposed to be associated with the ordinary electromagnetic field. It was found that in the periodic motion of a point-electron round a stationary nucleus the radiation to infinity of energy, linear momentum and angular momentum was such that when an average was taken for all directions and for a complete period, the average radiation was in each case zero. Unfortunately, this was not true for each direction and so the result was to some extent unsatisfactory. Attempts to modify the stress-energy tensor with a view to remedying this defect have so far proved unsuccessful[2] and so an attempt will now be made to alter the fields. Some alteration is, indeed, necessary, because, strictly, we are not entitled to represent an electron as a point charge. Moreover, as soon as the electron is treated as of finite size the question of the rate of spin becomes important, not only because the electron, when spinning, acts as a magnetic doublet, but also because a spin will undoubtedly alter the value of ψ.

[1] H. Bateman, Phys. Rev. **20**, 243 (1922).

[2] H. Bateman, Mess. of Math. **52**, 116 (1922); **53**, 145 (1924); **54**, 142 (1925); M. Salkover, Phys. Rev. **27**, 87 (1926).

Since the rotation and deformation of the electron are unknown we shall assume that the fields are unknown except in so far as they can be represented by retarded potentials of a certain type and shall look for the restrictions, if any, which must be laid on the electromagnetic field in order that there may be no radiation of energy and angular momentum to infinity in any direction.

The Radiation of Energy

2. The expressions suggested originally for the components of the tensor giving the distribution of energy and momentum and also their rates of flow were subsequently modified in order that the space outside an isolated stationary electron might be entirely free from stress. The components that have now been adopted[3] for the space outside all the electric charges are of types

$$X_x=\frac{1}{3}(E_x^2+H_x^2)-\frac{1}{6}(E^2+H^2)+\frac{2}{3}\left(\frac{\partial\psi}{\partial x}\right)^2-\frac{k}{8}\frac{\partial^2}{\partial x^2}(\psi^2)-\frac{4-3k}{12}\Gamma\,,$$

$$X_y=\frac{1}{3}(E_xE_y+H_xH_y)+\frac{2}{3}\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial y}-\frac{k}{8}\frac{\partial^2}{\partial x\partial y}(\psi^2)=Y_x\,,$$

$$W=\frac{1}{6}(E^2+H^2)-\frac{2}{3c^2}\left(\frac{\partial\psi}{\partial t}\right)^2+\frac{k}{8c^2}\frac{\partial^2}{\partial t^2}(\psi^2)-\frac{4-3k}{12}\Gamma\,,$$

$$S_x=\frac{1}{3}c(E_yH_z-E_zH_y)+\frac{2}{3}\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial t}-\frac{k}{8}\frac{\partial^2}{\partial x\partial t}(\psi^2)=c^2G_x\,,$$

where

$$\Gamma=\left(\frac{\partial\psi}{\partial x}\right)^2+\left(\frac{\partial\psi}{\partial y}\right)^2+\left(\frac{\partial\psi}{\partial z}\right)^2-\frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2$$

and $k=1$. If ψ satisfies the wave equation

$$\Box\psi\equiv\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}=0\,,$$

and the field vectors $\mathbf{E}$ and $\mathbf{H}$ satisfy Maxwell's equations

$$\operatorname{curl}\mathbf{H}=\frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}\,,\qquad \operatorname{div}\mathbf{E}=0$$

$$\operatorname{curl}\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{H}}{\partial t}\,,\qquad \operatorname{div}\mathbf{H}=0$$

[3] H. Bateman, Phil. Mag. **49**, 1 (1925). With these components the flow of energy in the field of an electron, which is moving uniformly, is at each point parallel to the line of motion of the electron. In the original paper we used the value $k=8/3$.

we have for any constant value of k

$$\frac{\partial X_x}{\partial x}+\frac{\partial X_y}{\partial y}+\frac{\partial X_z}{\partial z}-\frac{\partial G_x}{\partial t}=0\,,$$
$$\cdots\cdots\cdots\cdots\cdots$$
$$\frac{\partial S_x}{\partial x}+\frac{\partial S_y}{\partial y}+\frac{\partial S_z}{\partial z}+\frac{\partial W}{\partial t}=0\,.$$

Consequently if W represents the density of energy, S_x, S_y, S_z the components of the flow of energy, X_x, X_y, X_z, $\cdots$ the component stresses and G_x, G_y, G_z the densities of the components of linear momentum, we have conservation of energy and linear momentum in any finite portion of free space provided the flux across the boundary of the region is taken into consideration.

3. At a very great distance r from the center of an atom, which we take as our origin, the electromagnetic field may be written in the form

$$\mathbf{H}=-\frac{1}{c}\frac{\partial}{\partial t}\operatorname{curl}\mathbf{Q}+\operatorname{curl}\operatorname{curl}\mathbf{P}\,,\quad \mathbf{E}=-\frac{1}{c}\frac{\partial}{\partial t}\operatorname{curl}\mathbf{P}-\operatorname{curl}\operatorname{curl}\mathbf{Q}$$

where the vectors $\mathbf{Q}$ and $\mathbf{P}$ are given by the series

$$\mathbf{Q}=\frac{\mathbf{q}}{r}+\frac{\partial}{\partial x}\left(\frac{\mathbf{q}_1}{r}\right)+\frac{\partial}{\partial y}\left(\frac{\mathbf{q}_2}{r}\right)+\frac{\partial}{\partial z}\left(\frac{\mathbf{q}_3}{r}\right)+\frac{\partial^2}{\partial x^2}\left(\frac{\mathbf{q}_{11}}{r}\right)+\cdots$$
$$+2\frac{\partial^2}{\partial y\partial z}\left(\frac{\mathbf{q}_{23}}{r}\right)+\cdots$$
$$\mathbf{P}=\frac{\mathbf{p}}{r}+\frac{\partial}{\partial x}\left(\frac{\mathbf{p}_1}{r}\right)+\frac{\partial}{\partial y}\left(\frac{\mathbf{p}_2}{r}\right)+\frac{\partial}{\partial z}\left(\frac{\mathbf{p}_3}{r}\right)+\frac{\partial^2}{\partial x^2}\left(\frac{\mathbf{p}_{11}}{r}\right)+\cdots$$
$$+2\frac{\partial^2}{\partial y\partial z}\left(\frac{\mathbf{p}_{23}}{r}\right)+\cdots\,.$$

in which quantities $\mathbf{q}$, $\mathbf{q}_1$, $\mathbf{q}_2$, $\mathbf{q}_3$, $\mathbf{q}_{11}$, $\cdots$ $\mathbf{p}$, $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{p}_3$, $\mathbf{p}_{11}$, $\cdots$ are all functions of $\tau=t-r/c$. These quantities are supposed to be finite for all values of τ and their derivatives with respect to τ are supposed to be likewise finite. We shall imagine them to be simple trigonometrical functions but this restriction is not necessary. Since these quantities are all bounded we shall disregard them or treat them as constants in estimating the order of magnitude of an expression.

In calculating the radiation of energy and linear momentum we need only retain terms of order $1/r$ in the expressions for $\mathbf{E}$, $\mathbf{H}$ and ψ. Consequently, to this order we may write

$$\mathbf{H}=\mathbf{s}\times\mathbf{b}+\mathbf{s}\times(\mathbf{s}\times\mathbf{a})\,,\qquad \mathbf{E}=-(\mathbf{s}\times\mathbf{H})$$

where $\mathbf{s}$ is the unit vector with components $(x/r, y/r, z/r)$ and where

$$\mathbf{a}=\frac{1}{c^2r}\mathbf{p}''-\frac{1}{c^3r^2}(x\mathbf{p}_1'''+y\mathbf{p}_2'''+z\mathbf{p}_3''')+\cdots$$

$$\mathbf{b}=\frac{1}{c^2r}\mathbf{q}''-\frac{1}{c^3r^2}(x\mathbf{q}_1'''+y\mathbf{q}_2'''+z\mathbf{q}_3''')+\cdots$$

In these equations primes denote differentiations with respect to the argument $t-r/c$. The approximate expressions for $\mathbf{E}$ and $\mathbf{H}$ give

$$\mathbf{E}\times\mathbf{H}=\mathbf{s}[\mathbf{a}^2+\mathbf{b}^2-(\mathbf{a}\cdot\mathbf{s})^2-(\mathbf{b}\cdot\mathbf{s})^2+2\mathbf{s}\cdot(\mathbf{a}\times\mathbf{b})]$$

Assuming that

$$\psi=\frac{\kappa}{r}+\frac{\partial}{\partial x}\left(\frac{\kappa_1}{r}\right)+\frac{\partial}{\partial y}\left(\frac{\kappa_2}{r}\right)+\frac{\partial}{\partial z}\left(\frac{\kappa_3}{r}\right)+\cdots$$

$$=\frac{\kappa}{r}-\frac{1}{cr^2}(x\kappa_1'+y\kappa_2'+z\kappa_3')+\cdots$$

approximately, we find that the flow of energy in the direction of $\mathbf{s}$ is $\mathbf{S}$ where

$$\mathbf{S}=\frac{1}{3}c(\mathbf{E}\times\mathbf{H})+\frac{2}{3}\nabla\psi\frac{\partial\psi}{\partial t}-\frac{k}{4}\nabla\psi\frac{\partial\psi}{\partial t}-\frac{k}{4}\psi\nabla\frac{\partial\psi}{\partial t}$$

$$=\frac{1}{3}c\mathbf{s}\Big[\mathbf{a}^2+\mathbf{b}^2-(\mathbf{a}\cdot\mathbf{s})^2-(\mathbf{b}\cdot\mathbf{s})^2+2\mathbf{s}\cdot(\mathbf{a}\times\mathbf{b})$$

$$-\left(2-\frac{3k}{4}\right)\frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2+\frac{3k}{4c^2}\psi\frac{\partial^2\psi}{\partial t^2}\Big]$$

approximately. Now ψ can generally be chosen so that this expression vanishes. This is evidently possible when $k=0$ for then we have simply to choose ψ so that $(\partial\psi/\partial\tau)^2$ is a given positive function. When $k\neq 0$ we have to solve an equation of type

$$\left(2-\frac{3k}{4}\right)\left(\frac{\partial\psi}{\partial\tau}\right)^2-\frac{3k}{4}\psi\frac{\partial^2\psi}{\partial\tau^2}=\frac{1}{r^2}\left[f\left(\frac{x}{r},\frac{y}{r},\frac{z}{r},\tau\right)\right]^2$$

$$=[F(\tau)]^2 \text{ say.}$$

It seems likely that a solution exists only when $F(\tau)$ is subject to certain restrictions. A general existence theorem for this differential equation is hard to find but it is easy to see that there are many cases in which the equation possesses a real solution. To see this let us put

$$\psi=e^{\sigma}, \qquad F(\tau)=e^{\sigma}G(\tau)$$

When σ is given we can find F if it is possible to choose a real function G such that

$$\left(2-\frac{3k}{2}\right)\left(\frac{\partial\sigma}{\partial\tau}\right)^2-\frac{3k}{4}\frac{\partial^2\sigma}{\partial\tau^2}=[G(\tau)]^2 \tag{1}$$

The quantity on the left-hand side must thus be positive. Let us now alter the problem a little and endeavor to determine σ when G is given. We then have to solve a Riccatian equation

$$\left(2-\frac{3k}{2}\right)\rho^2-\frac{3k}{4}\frac{\partial\rho}{\partial\tau}=[G](\tau)^2$$

for $\rho=\partial\sigma/\partial\tau$. Putting

$$\rho=-\frac{3k}{8-6k}\cdot\frac{1}{u}\frac{du}{d\tau}$$

we have the linear differential equation

$$\frac{d^2u}{d\tau^2}=\frac{8u}{9k^2}(4-3k)[G(\tau)]^2$$

for the determination of u and this equation generally possesses a real solution when $G(\tau)$ is an analytic function. Since $G(\tau)$ is practically arbitrary the function $F(\tau)$ is also of a very general nature. The restriction which is introduced by the circumstance that $F(\tau)=e^{\sigma}G(\tau)$, where σ is a solution of (1) does not seem to be very great.

The Radiation of Angular Momentum

3. When the radiation of energy is zero for each direction the radiation of linear momentum is also zero for each direction since the components of linear momentum are proportional to the components of the flow of energy and the momentum travels in a radial direction.

The rate of flow in a radial direction of the z-component of angular momentum is

$$-\frac{1}{r}[x(xY_z-yX_z)+y(xY_y-yX_y)+z(xY_z-yX_z)]\ .$$

This will be zero for each direction if

$$E_r(xE_y-yE_x)+H_r(xH_y-yH_x)+\left(2-\frac{3}{4}k\right)\frac{\partial\psi}{\partial r}\left(x\frac{\partial\psi}{\partial y}-y\frac{\partial\psi}{\partial x}\right)$$
$$-\psi\frac{3k}{4r}\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}-1\right)\left(x\frac{\partial\psi}{\partial y}-y\frac{\partial\psi}{\partial x}\right)=0\ ,$$

where the suffix r is used to denote the radial component. Introducing the polar coordinates

$$z=r\cos\theta\ , \qquad x=r\sin\theta\cos\phi\ , \qquad y=r\sin\theta\sin\phi\ ,$$

we may write

$$x\frac{\partial\psi}{\partial y}-y\frac{\partial\psi}{\partial x}=\frac{\partial\psi}{\partial\phi}\ ,$$

$$x\left(z\frac{\partial\psi}{\partial x}-x\frac{\partial\psi}{\partial z}\right)-y\left(y\frac{\partial\psi}{\partial z}-z\frac{\partial\psi}{\partial y}\right)=r\sin\theta\frac{\partial\psi}{\partial\theta}\ .$$

So far as terms of order $1/r$ are concerned we may also write

$$\frac{\partial\psi}{\partial r}=-\frac{1}{c}\frac{\partial\psi}{\partial\tau}$$

Now E_r and H_r are both of order $1/r^2$ consequently we may retain only terms of order $1/r$ in calculating $(xE_y-yE_x)/r$ and $(xH_y-yH_x)/r$. In particular we may write

$$xE_y-yE_x=rH_z\ , \qquad xH_y-yH_x=-rE_z$$

$$\begin{aligned}x(zE_x-xE_z)-y(yE_z-zE_y)&=z(xE_x+yE_y+zE_z)-r^2E_z\\&=-r^2E_z\end{aligned}$$

$$x(zH_x-xH_z)-y(yH_z-zH_y)=-r^2H_z$$

Writing

$$H_z=-H_\theta\sin\theta\ , \qquad E_z=-E_\theta\sin\theta$$

$$H_\theta=E\cos\omega\ , \qquad E_\theta=E\sin\omega$$

$$rH_r=u\cos\omega+v\sin\omega\ , \qquad rE_r=u\sin\omega-v\cos\omega$$

we find that the radiation of energy and angular momentum will be zero for each direction if the following equations are satisfied.

$$\begin{aligned}E^2&=\left(2-\frac{3}{4}k\right)\frac{1}{c^2}\left(\frac{\partial\psi}{\partial\tau}\right)^2-\frac{3}{4c^2}k\psi\frac{\partial^2\psi}{\partial\tau^2}\\Eu&=\left(2-\frac{3}{4}k\right)\frac{1}{c}\frac{\partial\psi}{\partial\theta}\frac{\partial\psi}{\partial\tau}-\frac{3}{4c}k\psi\frac{\partial^2\psi}{\partial\theta\partial\tau}\\Ev\sin\theta&=\left(2-\frac{3}{4}k\right)\frac{1}{c}\frac{\partial\psi}{\partial\phi}\frac{\partial\psi}{\partial\tau}-\frac{3}{4c}k\psi\frac{\partial^2\psi}{\partial\phi\partial\tau}\end{aligned} \qquad (2)$$

We shall find it convenient to write

$$2-\frac{3}{4}k=\lambda\ , \qquad \frac{3}{4}k=\mu\ , \qquad \psi=c\alpha\ .$$

When we take into consideration the fact that each of the quantities E_θ, E_ϕ, H_θ, H_ϕ, rE_r, rH_r is of the form $f(\theta, \phi, \tau)/r$ Maxwell's equations in polar coordinates may be written

$$\frac{1}{c}\sin\theta\frac{\partial}{\partial t}(rE_r)=\frac{\partial}{\partial\theta}(\sin\theta\,H_\phi)-\frac{\partial H_\theta}{\partial\phi}$$

$$\frac{1}{c}\sin\theta\frac{\partial}{\partial t}(rE_\theta)=\frac{\partial H_r}{\partial\phi}-\frac{\partial}{\partial r}(r\sin\theta\,H_\phi)\equiv\frac{1}{c}\sin\theta\frac{\partial}{\partial t}(rH_\phi)$$

$$\frac{1}{c}\frac{\partial}{\partial t}(rE_\phi)=\frac{\partial}{\partial r}(rH_\theta)-\frac{\partial H_r}{\partial\theta}\equiv-\frac{1}{c}\frac{\partial}{\partial t}(rH_\theta)$$

. . . . . .

and give simply

$$E_\theta=H_\phi\,,\qquad E_\phi=-H_\theta$$

$$\frac{1}{c}\sin\theta\frac{\partial}{\partial\tau}(rE_r)=\frac{\partial}{\partial\theta}(\sin\theta\cdot E_\theta)-\frac{\partial H_\theta}{\partial\phi}$$

$$\frac{1}{c}\sin\theta\frac{\partial}{\partial\tau}(rH_r)=\frac{\partial}{\partial\theta}(\sin\theta\cdot H_\theta)+\frac{\partial E_\theta}{\partial\phi}$$

Substituting the values of E_θ, H_θ, rE_r, rH_r in terms of u, v, E and ω, we obtain

$$\left.\begin{aligned}\frac{1}{c}\sin\theta\left(\frac{\partial u}{\partial\tau}+v\frac{\partial\omega}{\partial\tau}\right)&=E\cos\theta+\sin\theta\frac{\partial E}{\partial\theta}+E\frac{\partial\omega}{\partial\phi}\\ \frac{1}{c}\sin\theta\left(\frac{\partial v}{\partial\tau}-u\frac{\partial\omega}{\partial\tau}\right)&=\frac{\partial E}{\partial\phi}-E\sin\theta\frac{\partial\omega}{\partial\theta}\end{aligned}\right\}\qquad(3)$$

Writing $\lambda\log\alpha-\mu\log\partial\alpha/\partial\tau=\beta$ and making use of the relations (2) we obtain the following differential equations for ω.

$$\left.\begin{aligned}\frac{1}{\sin\theta}\frac{\partial(\omega,\beta)}{\partial(\phi,\tau)}&=\frac{1}{2}\frac{\partial(\log\partial\beta/\partial\tau,\beta)}{\partial(\theta,\tau)}+\frac{\partial(\log\alpha,\log\partial\alpha/\partial\tau)}{\partial(\theta,\tau)}-\frac{\partial\beta}{\partial\tau}\cot\theta\\ \frac{\partial(\omega,\beta)}{\partial(\theta,\tau)}&=-\frac{1}{\sin\theta}\left[\frac{1}{2}\frac{\partial(\log\partial\beta/\partial\tau,\beta)}{\partial(\phi,\tau)}+\frac{\partial(\log\alpha,\log\partial\alpha/\partial\tau)}{\partial(\phi,\tau)}\right]\end{aligned}\right\}\qquad(4)$$

When $k=0$ we have $\beta=2\log\alpha$ and the equations for ω reduce to

$$\frac{\partial(\omega,\beta)}{\partial(\phi,\tau)}=-\frac{\partial\beta}{\partial\tau}\cos\theta\,,\qquad\frac{\partial(\omega,\beta)}{\partial(\theta,\tau)}=0\,,$$

The last equation gives

$$\omega=F(\beta,\phi)\,,$$

and when we substitute in the first equation we find that

$$\left(\frac{\partial F}{\partial \phi}+\cos\theta\right)\frac{\partial \beta}{\partial \tau}=0.$$

This equation gives a value of β which is independent of τ and so when $k=0$ there is no solution which is of physical interest. When $k\neq 0$ we may eliminate ω from the equations

$$\frac{\partial(\omega,\beta)}{\partial(\phi,\tau)}=\Theta\,,\qquad \frac{\partial(\omega,\beta)}{\partial(\theta,\tau)}=-\Phi \tag{5}$$

and obtain a partial differential equation for α. The result is

$$\Theta\frac{\partial^2\beta}{\partial\theta\,\partial\tau}+\Phi\frac{\partial^2\beta}{\partial\phi\,\partial\tau}=\frac{\partial\beta}{\partial\tau}\left[\frac{\partial\Theta}{\partial\theta}+\frac{\partial\Phi}{\partial\phi}\right]-\frac{\partial\beta}{\partial\theta}\frac{\partial\Theta}{\partial\tau}-\frac{\partial\beta}{\partial\phi}\frac{\partial\Phi}{\partial\tau}$$
$$+\frac{\dfrac{\partial^2\beta}{\partial\tau^2}}{\dfrac{\partial\beta}{\partial\tau}}\left[\Theta\frac{\partial\beta}{\partial\theta}-\Phi\frac{\partial\beta}{\partial\phi}\right]$$

where Θ and Φ have the values obtained by substituting (5) in (4). The general solution of this partial differential equation will probably be difficult to obtain. A particular solution may be obtained at once by assuming that α and ω are independent of ϕ. The equations (4) then give

$$\omega=f(\beta)$$

$$\frac{1}{2}\,\frac{\partial(\log\partial\beta/\partial\tau,\beta)}{\partial(\theta,\tau)}+\frac{\partial(\log\alpha,\log(\partial\alpha/\partial\tau)}{\partial(\theta,\tau)}=\frac{\partial\beta}{\partial\tau}\cos\theta$$

In this case the axis of z is an axis of symmetry for the fields and so from the point of view of Bohr's theory of the atom the fields are not of much physical interest.

Further discussion of the differential equation must be postponed until the nature of the solutions is better understood. Another differential equation which is more easily treated is obtained by considering the case in which

$$E^2=\frac{1}{c^2}\,\frac{\partial\Omega}{\partial t}\,,\qquad Eu=\frac{1}{c}\,\frac{\partial\Omega}{\partial\theta}\,,\qquad Eu\sin\theta=\frac{1}{c}\,\frac{\partial\Omega}{\partial\phi}\,.$$

Substituting in equations (3) we find that if $\chi=\log(\operatorname{cosec}^2\theta\cdot\partial\Omega/\partial\tau)$

$$\operatorname{cosec}\theta\frac{\partial(\omega,\Omega)}{\partial(\phi,\tau)}=\frac{1}{2}\frac{\partial(\chi,\Omega)}{\partial(\theta,\tau)}$$

$$\frac{\partial(\omega,\Omega)}{\partial(\theta,\tau)}=-\frac{1}{2}\operatorname{cosec}\theta\frac{\partial(\chi,\Omega)}{\partial(\phi,\tau)}$$

Writing

$$\omega+\frac{1}{2}i\log\left(\frac{\partial\Omega}{\partial\tau}\operatorname{cosec}^2\theta\right)=\alpha\,,\qquad\omega-i\chi=\beta$$

$$\sigma=\log\tan\frac{1}{2}\theta+i\phi\,,\qquad\rho=\log\tan\frac{1}{2}\theta-i\phi$$

we have

$$\frac{\partial(\alpha,\Omega)}{\partial(\sigma,\tau)}=0\,,\qquad\frac{\partial(\beta,\Omega)}{\partial(\rho,\tau)}=0\,,$$

These equations are satisfied by

$$\alpha=i\log f[\Omega,\sigma]$$

$$\beta=-i\log f[\Omega,\rho]$$

where f is an arbitrary function of its two arguments. We finally obtain

$$\partial\Omega/\partial t=\sin^2\theta\,f[\Omega,\log\tan\tfrac{1}{2}\theta+i\phi]f[\Omega,\log\tan\tfrac{1}{2}\theta-i\phi]\,,$$

This may be regarded as a partial differential equation for the determination of Ω. This partial differential equation may be solved in a large number of cases.

The electromagnetic field determined by a function Ω of this type is particularly interesting because the rate of radiation of energy is a time derivative and so the total radiation in any interval of time may be expressed as the difference of the initial and final values of a certain quantity. The rate of radiation of the z-component of angular momentum may, too, be expressed in a simple form, for in the integral

$$\int_0^{\pi}\int_0^{2\pi}(\partial\Omega/\partial\phi)\sin\theta\,d\theta\,d\phi$$

the integration with respect to ϕ may be performed at once. If the function Ω is single-valued in ϕ, there is no radiation of this component.

If it ever becomes possible to describe the properties of radiation on the basis of the classical electromagnetic theory alone this type of field may be of some interest.

Remarks on the Classical Theory

4. A new attempt to solve the radiation problem on the basis of Maxwell's electromagnetic equations has been made recently by N. v. Raschevsky.[4] His work possesses some good features inasmuch as an attempt is made to find a field which first gives no radiation in a stationary state, then passes over into a state in which there is radiation and finally returns to another stationary state in which there is no radiation. His field which gives no radiation is represented by means of integrals of Kirchhoff's type including surface integrals one of which is practically the potential of a double layer. Now in ordinary potential theory the potential of a double layer is discontinuous at the layer itself. Consequently one is left with the impression that Raschevsky's field is not really a continuous field. This is a defect but may not be a fatal objection to the theory because the discontinuity may simply mean that the ordinary Maxwell field-equations break down in the immediate vicinity of an atom when the fields are very strong. There may be equations something like Maxwell's but the relations

$$\mathbf{D}=\mathbf{E}\,, \qquad \mathbf{B}=\mathbf{H}$$

expressing a simple proportionality between stress and strain may no longer hold. Like the solution proposed by Dr. H. A. Lorentz, in his lectures at Pasadena, Raschevsky's solution has the advantage of giving no radiation in any direction at any instant and since the field vectors are of order $1/r^2$ at a great distance from the origin, there is no radiation of angular momentum.

5. Like most writers Raschevsky takes a vibrating electric dipole as a model of an electromagnetic radiator. The radiation of angular momentum in the field of a dipole has been calculated by several writers[5] and Rubinowicz has used the results to formulate a selection principle in quantum theory.

A point that seems rather puzzling is that when the dipole rotates like a rigid body the angular momentum about the z-axis is radiated not in the direction of the axis, the direction in which the light is circularly polarized, but chiefly in the neighborhood of the plane of rota-

[4] N. v. Raschevsky, Zeits. f. Physik **35**, 100 (1925).

[5] For the literature see W. H. Westphal, Jahrb. d. Radioaktivität. **18**, 105 (1921).

tion and in directions in which the light is linearly polarized. As Ehrenfest pointed out, the theory of the Hertzian dipole gives no support to Poynting's idea that circularly polarized light is accompanied by angular momentum.

The radiation of angular momentum in the field of the vibrating diplole is seen to depend on the fact that the flow of energy is strictly not in a radial direction and that consequently there is a moment arm from the origin to the line of flow. The length of this perpendicular may be found as follows:

Let us take $\mathbf{P}=0$, $r\mathbf{Q}=\mathbf{q}(t-r/c)$, then, retaining terms of orders $1/r^2$ and $1/r^3$ we have

$$E^2=H^2=\frac{r^2\mathrm{q}''^2-(\mathbf{r}\cdot\mathrm{q}'')^2}{c^4r^4}+2\,\frac{r^2(\mathrm{q}'\cdot\mathrm{q}'')-(\mathbf{r}\cdot\mathrm{q}')(\mathbf{r}\cdot\mathrm{q}'')}{c^3r^5}$$

$$\mathbf{E}\times\mathbf{H}=\mathbf{s}\left[E^2-\frac{2(\mathbf{r}\cdot\mathrm{q}')(\mathbf{r}\cdot\mathrm{q}'')}{c^3r^5}\right]+\frac{2\mathrm{q}''(\mathbf{r}\cdot\mathrm{q}')}{c^3r^4}$$

Using ϖ to denote the length of the perpendicular from the origin to the line of flow, we have

$$\varpi^2=\frac{[\mathbf{r}\times(\mathbf{E}\times\mathbf{H})]^2}{E^2}=\frac{4(\mathbf{r}\cdot\mathrm{q}')^2}{c^6r^8E^4}[\mathbf{r}^2q''^2-(\mathbf{r}\cdot\mathrm{q}'')^2]$$

Replacing E^2 by its approximate value

$$\frac{1}{c^4r^4}[r^2q''^2-(\mathbf{r}\cdot\mathrm{q}'')$$

we find that

$$\varpi^2=\frac{4c^2(\mathbf{r}\cdot\mathrm{q}')^2}{r^2q''^2-(\mathbf{r}\cdot\mathrm{q}'')^2}$$

When

$$q_x=a\cos 2\pi\nu\tau\,,\qquad q_y=a\sin 2\pi\nu\tau\,,\qquad q_z=0\,,$$

we have

$$\varpi^2=\frac{c^2}{\pi^2\nu^2}\,\frac{(y\cos 2\pi\nu\tau-x\sin 2\pi\nu\tau)^2}{z^2+(y\cos 2\pi\nu\tau-x\sin 2\pi\nu\tau)^2}$$

This formula indicates that ϖ lies between zero and $c/\pi\nu$; it is zero on the axis of z when $x=y=0$ and has its maximum value in the plane $z=0$.

A line drawn through the point (x, y, z) in the direction of Poynting's vector will, to the present order of approximation, meet the plane of xy in a point whose coordinates are

$$X = J \cos 2\pi\nu\tau\ , \qquad Y = J \sin 2\pi\nu\tau$$

where

$$J = \frac{c\tau}{\pi\nu} \frac{(y \cos 2\pi\nu\tau - x \sin 2\pi\nu\tau)}{z^2 + (y \cos 2\pi\nu\tau - x \sin 2\pi\nu\tau)^2}$$

approximately. Eliminating τ we obtain the equation

$$\frac{\pi\nu z^2}{c\tau}(X^2 + Y^2) + (yX - xY)\left(yX - xY - \frac{c\tau}{\pi\nu}\right) = 0$$

The lines of motion which pass through the point (x, y, z) thus generate a quadric cone.

DEPARTMENT OF MATHEMATICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA,
February 12, 1926.

MEAN INTENSITY OF SOUND IN AN AUDITORIUM AND OPTIMUM REVERBERATION

By Samuel Lifshitz

Abstract

The optimum time of reverberation was determined experimentally for the piano, the violin, the violoncello, for bass and soprano voices and human speech in a room of 260 m³. The experimental determinations (1.08-1.14 sec.) give the mean value of 1.11 sec. An earlier investigation in a smaller hall of 126 m³ gave a mean optimum time of $T_{op}=1.06$ sec. It is evident that a mean intensity of sound exists which is the same for human speech and musical performances of different kinds, with respect to which our ear determines the optimum of the impression. The value of this intensity (10^{6n} times minimum audible intensity, i) is given by the formula: $1.333n+\log_{10}(aS_1)=3.07$. For $aS_1=49.5$, the mean intensity is equal to $10^{6.019}$. From this, we have as the formula for the optimum time of reverberation, for a room of W m³ volume:

$$\log_{10}W=8.5+\log_{10}T_{op}-\frac{6.194}{\sqrt[2]{T_{op}}}.$$

CONSIDERING the importance of the experimental determination of the optimum time of reverberation, we have verified again, in a different room, the conclusion that the optimum for the same hall is identical for different musical performances and speech.

The investigation was conducted in the concert hall of the State Institute of Musical Science in Moscow. This hall has a volume of 265m³ and seats 120 persons. The reverberation for the empty hall is 2.63 seconds. During the musical performances, we changed the number of auditors and, by this means, determined the optimum of reverberation. Instead of a piano, we made use of an automatic performer, the so-called "Mignon-piano," so that the music and its performance could be repeated identically for different conditions of the experiment. Results obtained are as follows:

Source	Optimum reverberation
piano	1.13 sec.
violin	1.11 sec.
violoncello	1.11 sec.
bass voice	1.11 sec.
soprano voice	1.11 sec.
human speech[1]	1.14–1.08 sec.
mean (T_{op})	=1.11 sec.

[1] For speech, we determined the optimum when the finest quality of the voice was obtained. Further decreases in the reverberation increased the clearness of speech, but the quality of the voice sounded dry. See V. O. Knudsen, Phys. Rev. **26**, 287 (August, 1925).

Our previous investigations[2] gave a mean value of 1.03 sec. The mean value obtained by Wallace Sabine[3] was 1.08 sec., while a similar value found by Watson[4] was 1.04 sec. The average of all these mean values is 1.06 sec., as found in the previous investigation, and gives the optimum reverberation for music and speech for the investigated small halls with volumes varying from 74 to 260 m³. We can explain this result if we assume that a constant mean intensity of sound exists for different kinds of music and speech, with respect to which our ear determines the quality of the music heard.

The following considerations give us the meaning of the average acoustic intensity. Let the optimum time (1.05 sec.) hold for a hall of less than W_1 m³. For smaller halls, the optimum can remain constant because the performer appropriately diminishes the loudness of his

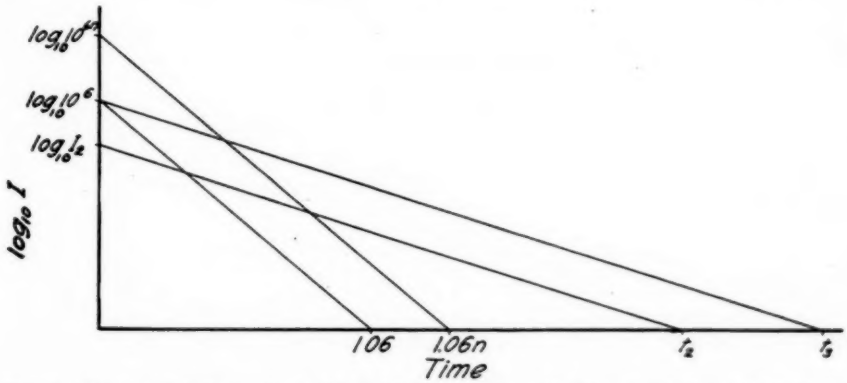

Fig. 1. Showing relative values of t and $\log I$, based on the linear relation, $at = 2.3 \log_{10} (I_0/i)$, derived from the reverberation equation: $i = I_0 e^{-at}$.

voice or musical instrument to suit the conditions of the room. Let the absorption of the hall $W_1 = aS_1$ and the mean intensity of sound be given by $I_1/i = 10^{6n}$ (where i is the threshold intensity and n is variable depending on conditions. For $n = 1$, $I_1/i = 10^6$); the actual reverberation therein will be equal to $1.06n$ sec. In the larger room W_2, with the absorption equal to aS_2, the mean intensity of sound will be less; or $I_2/i = 10^{6n} aS_1/aS_2$. The actual reverberation will be t_2 seconds; the reverberation corresponding to the standard intensity, $I_0/i = 10^6$, will be t_3.

If we want to get a good musical impression in a larger room with a smaller intensity of sound, it is assumed necessary to have a longer

[2] Lifshitz Phys. Rev. **25**, 391 (March, 1925).
[3] Wallace Sabine, "Collected Works," page 75.
[4] F. R. Watson, "Acoustics of Buildings," page 51.

time of reverberation. That is, the energy of musical perception must be constant, or

$$t \log_{10} I = \text{constant}. \tag{1}$$

(The intensity is perceived, according to Weber-Fechner's law, in proportion to its logarithm.)[5]

In our case of the two halls W_1 and W_2, the equation will take the form:

$$t_2 \log_{10} I_2 = 6.36n^2 .$$

From Fig. 1, we have by similar triangles:

$$t_2 : t_3 = \log_{10} I_2 : \log_{10} 10^6$$

or

$$t_2 = t_3 (\log_{10} I_2)/6$$

and on the basis of (1), we can write:

$$t_3^{\frac{1}{2}} \log_{10} I_2 = 6.175n$$

$$\log_{10} I_2 = \log_{10}(10^{6n} aS_1/aS_2).$$

Substituting we have:

$$t_3^{\frac{1}{2}}[6n + \log_{10}(aS_1) - \log_{10}(aS_2)] = 6.175n. \tag{2}$$

Let us substitute in the last equation the acoustic data for a perfect hall. As an example of such a hall we can take the Column Hall of the House of Unions in Moscow. This hall has a volume of 12,500 m³.

$$T_{op} = 1.75 \text{ sec.}, \qquad aS_2 = 1175.$$

Then we have:

$$1.333n + \log_{10}(aS_1) = 3.07 \tag{3}$$

where $aS_1 = .164W_1/1.06$. Eq. (3) gives the relation between n and the maximum volume W_1 for which the optimum time of reverberation of 1.06 sec. holds. According to our previous supposition, ($n = 1$ for $I = 10^6 i$), the volume $W_1 = 350$ m³.

Paul Sabine[6] takes $\log_{10} I = (9.1 - \log_{10} a)$ in English units, basing this on his experiments on the intensity of the sound of the voice and instruments; from which, according to (3)

$$n = 1.07 ; \qquad W_1 = 285 \ m^3 ; \qquad I = 10^{6.42}.$$

[5] Vern O. Knudsen, Phys. Rev. **21**, 84 (1923).

[6] Paul Sabine. "Acoustics in Auditorium Design," Amer. Archt., June, 1924.

Considering the small difference between Sabine's values and those obtained by the author, we take for the mean volume: $W_1 = 320$ m³, from which

$$n = 1.0032 \text{ and } I/i = 10^{6.019}.$$

Later, when the optimum time of reverberation is investigated for a larger number of rooms and the determinations made for n and W_1, for which the closest coincidence occurs with experimental results, we shall have more exact values. Substituting our determinations for n and W_1 in the formula (2), we have the equation for the optimum time, T_{op}

$$\log_{10} W = 8.5 + \log_{10} T_{op} - \frac{6.194}{\sqrt{T_{op}}}. \qquad (4)$$

This equation is more exact than my previous one,[2] but it differs from it numerically by the amount of experimental errors.

In comparison with the results of my measurements of Russian halls, I give data for some American halls:[4]

	Volume in m³	Full number of people present	Reverberation of full hall	Optimum according to (4) "perfect acoustics"
1. Munic. Audt.	31000		2.13 sec.	2.05 sec.
2. Gt. Hall, Coll. N. Y.*	23400		1.97 sec.	1.96 sec.
3. Eastman Theatre	22400	3340	2.08 sec.	1.95 sec.
4. Boston Music Hall	18300	2471	2.31 sec. (rather loud, 22%)	1.88 sec.
5. Leipzig Gewandhaus	11400	1597	2.30 sec. (rather loud, 35%)	1.73 sec.
6. Detroit Orch. Hall	8350		1.55 sec.	1.65 sec.
7. Smith Concert Hall	6550	1042	1.67 sec.	1.60 sec.
8. Apollo Theatre	5900	1670	1.34 sec. ("dry", perfect for 1235 persons)	1.57 sec.
9. Kilbourn Hall	3960	510	1.65 sec. (satisfactory, rather loud)	1.50 sec.
10. Wesley Auditorium	2860	500	1.16 sec. ("dry", perfect for 300 persons)	1.42 sec.
11. Little Theatre	1730		1.28 sec.	1.32 sec.

THE PHYSICAL INSTITUTE OF THE UNIVERSITY OF MOSCOW,
STATE INSTITUTE OF MUSICAL SCIENCE,
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ROTATION OF THE PULLEY IN MELDE'S EXPERIMENT

By Arthur Taber Jones

Abstract

The apparently continuous rotation which may sometimes be observed in the pulley in Melde's experiment is assumed to be the result of a succession of small slips of the pulley under the string near some particular phase of the motion. The *equations of motion* are solved under the assumptions that there is no transverse vibration of the string, that the string does not slip on the pulley, that there is no damping, and that the motion is simple harmonic with a frequency equal to that of the tuning fork. It is shown that any slipping will first occur when the pulley is close to an end of its swing, and from this it follows that the sense of a net rotation is determined by the particular end of the swing at which this slipping occurs. The theory indicates that the sense of the rotation depends on the length of the vertical part of the string, but is independent of the length of the horizontal part. In experimental tests of the above theory, the senses of rotation observed for different lengths of the vertical part of the string agree with the theory in a great many cases, but differ in so many other cases as to show that the theory needs modification—probably by taking account of damping. The string used shows considerable elastic after effect, and its *modulus of elasticity* increases with the load. Values of the elastic modulus calculated from the lengths at which the rotation of the pulley reversed show a moderately good agreement with directly determined values. Values of the coefficient of friction between string and pulley, calculated from the amplitude of the pulley when rotation began, are in fair agreement with values which were found directly.

Introduction

IN Melde's beautiful experiment[1] a tuning fork sets up standing waves in a string. The string often runs horizontally from the fork to a pulley and then downward to a point where it may be fastened or may carry a small load. Raman and Apparao,[2] A. W. Porter,[3] and J. S. Stokes,[4] independently discovered that the pulley may sometimes appear to rotate continuously. The rotation requires the fork so placed as to set up a longitudinal vibration in the string, but transverse vibration may or may not be present. Stokes found that under certain circumstances a little beeswax applied to the part of the string in contact with the pulley reversed the rotation, and a drop of kerosene in the groove in the pulley restored the original rotation.

[1] F. Melde, Pogg. Ann. **109**, 192 (1859); **111**, 513 (1860); Wied. Ann. **21**, 452 (1884); **24**, 497 (1885).

[2] C. V. Raman, Phys. Rev. **32**, 307 (1911).

[3] A. W. Porter, Knowledge and Scientific News, **5**, 193 (1908).

[4] J. S. Stokes, Phys. Rev. **30**, 659 (1910).

Shortly after Stokes's discovery I found it possible to reverse the rotation without wax or kerosene. Sometimes forcing a change in the length of the vibrating segment next to the pulley led to a reversal, and sometimes a slight change in the tension of the string sufficed. I also found that if the string passed over two pulleys there might be a rotation of both. This study was very incomplete, and the results were not published. In a joint article[5] several years later I published a few additional facts, and shortly afterward a suggestion[6] as to the general explanation of the rotation. The present paper, restricted to the case where there is no transverse vibration of the string, makes a beginning at a more complete theory of these phenomena, and gives some experimental tests of the theory.

THEORY

Cause of rotation. The explanation of the rotation is doubtless to be found in a slipping between the pulley and the string at some particular phase of the motion. Now when a string is on the point of slipping along a curved surface it is well known that the tensions, T_1 and T_2, in the free ends of the string are connected by the relation

$$T_2 = T_1 e^{\mu\varphi} , \tag{1}$$

where μ stands for the coefficient of friction, and φ for the supplement of the angle made by the free parts of the string. If the tensions vary, and the angle between the free parts of the string does not change, the string slips when the ratio of the tensions becomes sufficiently great.

In considering Melde's experiment let us deal only with the case where there is no transverse vibration of the string, and let us for the present assume that the string does not slip on the pulley. Let the tensions (Fig. 1) be given by the equations

$$T_l = T_0 + L \cos pt$$

and

$$T_h = T_0 + H \cos pt ,$$

and let both L and H be smaller than T_0. Set $L = H + S$. Then

$$T_l / T_h = 1 + S \cos pt / (T_0 + H \cos pt) .$$

This ratio attains its extreme values when $pt = 0$ and $pt = \pi$. Moreover, the ratio of the larger tension to the smaller has different values when $pt = 0$ and when $pt = \pi$. These facts mean that when the ampli-

[5] A. T. Jones and M. E. Phelps, Phys. Rev. **10**, 544 (1917).
[6] A. T. Jones, Phys. Rev. 11, 150 (1918).

tude of the pulley becomes sufficient for slipping to begin, it begins with the pulley at an end of its swing, and at one end rather than at the other. It follows that there is a succession of small slips, all in one direction, and if the frequency is sufficient this succession of small net rotations looks as if it were one continuous rotation.

General method of determining sense of rotation. If we examine the various possible cases as to the signs of L, H, and S, we find that the ratio of the larger tension to the smaller is greater at that end of the swing at which the tension which varies most has its smallest value. To determine the sense of the rotation of the pulley we therefore ask first in which part of the string the variation in tension is the greater.

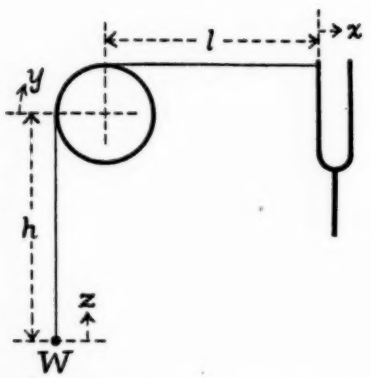

Fig. 1. Meaning of symbols. A rotation in the sense of the arrow y is called *rotation toward* the fork, and rotation in the opposite sense is called *rotation away* from the fork.

Choosing that part of the string, we then find the position of the pulley when the tension in that part of the string is the least. If this occurs when the pulley is at the end of a swing toward the fork, any slipping will allow it to swing on a little farther toward the fork, and there will be a net of rotation toward the fork. Similar statements apply for rotation away from the fork.

End of string fastened. Let the end of the string at W (Fig. 1) be fastened. Let the amplitude of the pulley be so small that there is no slipping, and consequently no net rotation. To simplify matters let us also neglect damping. Let l and h stand for the lengths of the horizontal and vertical parts of the string, both of them measured when the fork and pulley are in their equilibrium positions, and let l_0 and h_0 stand for the unstretched lengths of these same parts of the string. Let x stand for the displacement of the end of the prong of the fork,

and y for the displacement of a point in the groove of the pulley. Then the tensions in the two parts of the string are

$$T_l=\lambda(l+x-y-l_0)/l_0 \tag{2}$$

and

$$T_h=\lambda(h+y-h_0)/h_0 , \tag{3}$$

where λ stands for the elastic modulus of the string. When the system is in its equilibrium position, $x=y=0$ and $T_l=T_h$, so that (2) and (3) give

$$\lambda(l-l_0)/l_0=\lambda(h-h_0)/h_0 . \tag{4}$$

Let θ stand for the angular displacement of the pulley, I for its moment of inertia, and r for the radius of the groove. Then

$$\theta=y/r , \tag{5}$$

and since we are neglecting damping,

$$(T_l-T_h)r=I\ddot{\theta} , \tag{6}$$

From the five equations (2)-(6) it turns out to be possible to eliminate the five quantities T_l, T_h, l, h, and θ. We obtain

$$\ddot{y}+n^2y=r^2\lambda x/Il_0 , \tag{7}$$

where

$$n^2=\frac{r^2\lambda}{I}\left(\frac{1}{l_0}+\frac{1}{h_0}\right) . \tag{8}$$

Let the motion of the fork be given by

$$x=a\cos pt , \tag{9}$$

where $a>0$, and assume that the pulley rocks with a motion

$$y=b\cos pt . \tag{10}$$

On eliminating x and y from (7), (9), and (10), we find that b is determined by

$$b=\frac{r^2\lambda}{Il_0}\cdot\frac{a}{n^2-p^2}=\frac{h_0a}{h_0+l_0-p^2Ih_0l_0/r^2\lambda} . \tag{11}$$

Thus the phase of the pulley is the same as that of the fork or opposite to it according as h_0+l_0 is greater or less than $p^2Ih_0l_0/r^2\lambda$.

To find which part of the string experiences the greater change in tension, eliminate x, y, and a from (2), (3), (9), (10), and (11). We get

$$T_l=\frac{l-l_0}{l_0}\lambda+\frac{\lambda b}{h_0}\left(1-\frac{p^2Ih_0}{r^2\lambda}\right)\cos pt \tag{12}$$

and

$$T_h = \frac{h-h_0}{h_0}\lambda + \frac{\lambda b}{h_0}\cos pt \ . \tag{13}$$

From (12) and (13) we see that T_l has a greater range than T_h if

$$h_0 > 2r^2\lambda/p^2I \ , \tag{14}$$

and a smaller range if the inequality (14) is reversed.

On following out the method indicated above for determining the sense of rotation, we are led through a somewhat complicated series of special cases to this remarkably simple result: If (14) is satisfied, any rotation of the pulley is toward the fork; and if (14) is reversed, any rotation is away from the fork. This means that *if the end of the string is fastened, the sense of the rotation is independent of the length of the horizontal part of the string, the rotation is toward the fork when the vertical part of the string is sufficiently long, and the rotation is away from the fork when the vertical part of the string is sufficiently short.*

End of string loaded. Instead of having the end of the string fastened at W (Fig. 1), let it carry a load which has mass m and displacement z. Assume that the load has a simple harmonic motion of the same frequency as the fork. Since we are neglecting damping, the phase of the load must be either the same as that of the fork or opposite to that of the fork, and we may write

$$z = c\cos pt \ . \tag{15}$$

We obtain various equations which correspond to those that we used when the end of the string was fastened, but we find that we need an additional relation, and that this new relation may be obtained by regarding the load and the vertical part of the string as executing a forced vibration under the action of the pulley. After setting up this new relation, and then proceeding in a manner similar to that which we followed before, we finally obtain

$$b = a/\{1+l_0[(h_0-\lambda/mp^2)^{-1}-Ip^2/\lambda r^2]\} \ , \tag{16}$$

$$T_l = mg+\lambda b[(h_0-\lambda/mp^2)^{-1}-Ip^2/\lambda r^2]\cos pt \ , \tag{17}$$

and

$$T_h = mg+\lambda b(h_0-\lambda/mp^2)^{-1}\cos pt \ . \tag{18}$$

In this case we see that T_l has a greater range than T_h if $Ip^2/\lambda r^2 > 2/(h_0-\lambda/mp^2)$, i. e., if h_0 lies outside of the region given by

$$\lambda/mp^2 < h_0 < (1+2mr^2/I)\lambda/mp^2 \ ; \tag{19}$$

and that if h_0 lies inside of this region, it is T_h that has the greater range.

On carrying through the work to determine the sense of rotation we arrive again at a remarkably simple result: If h_0 lies inside of the region given by (19), any rotation of the pulley is away from the fork; whereas if h_0 lies outside of this region, the rotation is toward the fork. This means that *if the end of the string is loaded, the sense of rotation is independent of the length of the horizontal part of the string, and the rotation is toward the fork when the vertical part of the string is either sufficiently short or sufficiently long, and is away from the fork when the vertical part of the string has intermediate lengths.*

EXPERIMENT

Apparatus. In the present work I have used only one pulley, one string, and one frequency. The pulley is a brass one with cone bearings. Its radius is about 1.35 cm, and its moment of inertia about 19.0 g.cm^2. The string is the same braided fish cord that was used in previous work,[5,6] and has a linear density of about 2.24 mg/cm. The fork to which the string was attached is marked with a frequency of 100 double vibrations in a second, and was electrically driven by a second fork of the same frequency equipped with a mercury interrupter. When the amplitude of the fork was desired it was determined by reading in a micrometer microscope the width of a brightly illuminated line on the end of the prong to which the string was attached.

When transverse vibrations appear, it is sometimes possible to damp them out by holding one or two fingers lightly against the string. I have assumed that this procedure does not seriously affect the longitudinal vibration. There are however conditions under which the transverse vibrations are so strong that it is difficult to damp them out and feel sure that observations really represent what would happen if the vibration were purely longitudinal. Such cases are of course not included in my results.

General distribution of rotations. The theory indicates that the sense of rotation should be independent of the length of the horizontal part of the string. I have no observations which test this point. It is much easier to avoid transverse vibration in the horizontal part of the string when that part is short, and during a considerable part of the experimental work the length of the horizontal part of the string was between 4 cm and 5 cm.

When the end of the string is fastened, the theory indicates rotation toward the fork for the greater lengths of the vertical part of the string, and away from the fork for the smaller lengths. Experiment verified this prediction when the tension was 25 g, 30 g, or 35 g, but not when the tension was 5 g or 10 g.

When the end of the string is loaded, the theory indicates rotation away from the fork for intermediate lengths of the vertical part of the string, and toward the fork when the length is greater or smaller. Here again, observations with the smallest loads were either not consistent or not in agreement with the theory. But with loads of 20 g, 25 g, and 30 g, the various series of observations were pretty uniform in showing a rotation toward the fork for the greater lengths of the vertical part of the string, and away from it for the shorter. Rotation toward the fork for still shorter lengths was observed only twice, and neither of these observations is very reliable.

Elastic modulus of the string. If the end of the string is fastened, (14) shows that the rotation of the pulley reverses when

$$h_0 = 2r^2\lambda/p^2I \ ; \tag{20}$$

and if the string carries a load, (19) shows that there is a reversal when

$$h_0 = (1+2mr^2/I)\lambda/mp^2 \ . \tag{21}$$

A fair approximation to the value of the h_0 in (20) or (21) can be obtained by adjusting the vertical part of the string until it has the shortest length for which rotation is toward the fork, and again until it has the greatest length for which rotation is away from the fork. The mean of these two may be taken as not far from h_0. (20) or (21) may then be used to calculate λ.

To determine λ directly, the string was hung from the ceiling, a point near the lower end was observed in a micrometer microscope, and a load on the bottom of the string was changed. It very soon became evident that the string took considerable time to adjust itself to a new load. In one case readings for the elongation after adding a load of 100 g were made for an hour, and at the end of that time the string was still stretching, and there was no indication that the stretching was nearly complete. Removal of all of the load except 10 g was followed by a similar slow recovery. The curves showing change of length against time were of the shape which is customary in cases of elastic after effect.

When there is an appreciable elastic after effect, values obtained for the elastic moduli depend on the time for which the changed load acts. I attempted to get values for the elastic modulus by alternately adding and removing a given load, and allowing several minutes after a change of load before taking any readings. This method did not lead to consistent results—perhaps partly because of irregular changes

in the distance between the ceiling and the table on which the microscope rested.

The method finally adopted was to make a series of readings as rapidly as possible. A considerable aid in rapid reading was a camel's hair pencil which was mounted so as to rest lightly against the string just below the microscope, thus damping the swinging that was introduced when changing the load. A given increase was made in the load, the microscope read, the load decreased by an equal amount, the microscope read, the load again increased, and so on, until some forty or fifty readings had been made. This could be done in a little over half an hour, so that the elastic modulus was being determined for a force which varied at a rate a little slower than one cycle in a minute. Fig. 2

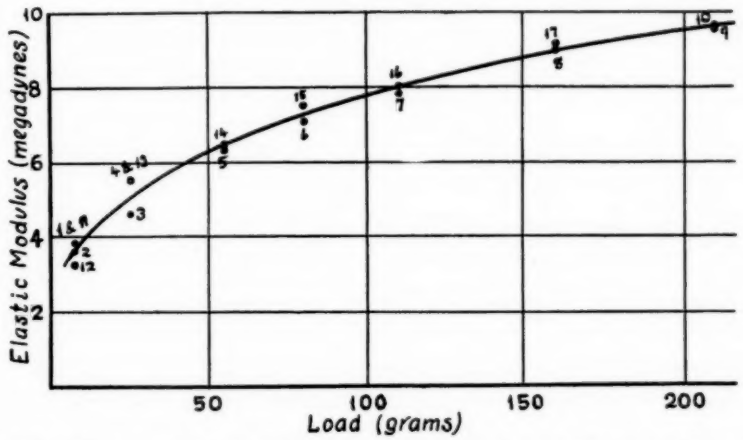

Fig. 2. Elastic modulus of the string as a function of the load. The numbers beside the plotted points give the order in which the values were obtained.

shows that the elastic modulus thus found for this braided cord is not independent of the tension—an effect which is probably to be explained by a straightening of the individual strands under the action of the heavier load.

A comparison of theoretical and directly determined values of the elastic modulus is shown in Table I. The reversal of the rotation usually occurred with h_0 in the neighborhood of 25 cm. A third of the theoretical values in the table are the results of single determinations; the rest are means from two or three determinations. It will be seen that the theoretical values are at least of the right order of magnitude. For the smaller loads the agreement is probably as good as could be expected.

Whether the fact that the theoretical values are in most cases smaller than the observed has any significance is doubtful. In the

cases of metals it is known[7] that the elastic moduli usually come out a little larger when determined dynamically than when determined statically. Wertheim[7] supposed that this difference was caused by the adiabatic heating and cooling in the dynamic experiments, and Kohlrausch[8] pointed out that any elastic after effect would also cause a difference in the same direction. In my results the difference is usually in the opposite direction, but it is very possible that when the theory has been extended so as to take account of the damping, the sign of the difference may be reversed. At any rate, the theoretical and the directly determined values agree much better than would have been supposed from the results on the general distribution of the positions for rotation in each sense.

TABLE I

Comparison between calculated and observed values for elastic modulus

Tension (grams)	End fastened Modulus (megadynes) calc.	obs.	Diff. %	End loaded Modulus (megadynes) calc.	obs.	Diff. %
15				41.5	43.0	−3.5
20				44.3	47.0	−5.7
25	48.4	50.7	−4.5	52.5	50.7	+3.6
30	43.8	54.0	−18.9	50.2	54.0	−7.0
35	49.5	56.7	−12.7	64.9	56.7	+14.5
40				50.6	59.2	−14.5

Friction between string and pulley. When the end of the string is loaded and there is no slipping of the string along the pulley, it will be seen from (16), (17), and (18) that if we know the elastic modulus of the string and observe the amplitude of the fork, we can calculate the tensions in both parts of the string. If we gradually increase the amplitude of the fork until slipping just begins—that is, until the pulley just begins to rotate—(17) and (18) give the limiting values of the tensions which we need in order to obtain from (1) a value for the coefficient of friction. A similar calculation can be made when the end of the string is fastened.

No observations were made for the purpose of determining the coefficient of friction. But in various cases the amplitude was increased by steps, and the rotation or lack of rotation was recorded for each amplitude. From these records there were selected for calculating the

[7] G. Wertheim, Pogg. Ann., Erg.-Bd. **2**, 1 (1848).
E. Warburg, Wied. Ann. **10**, 13 (1880).
Theodor Schröder, Wied. Ann. **28**, 369 (1886).
George A. Lindsay, Phys. Rev. **3**, 397 (1914).

[8] F. Kohlrausch, Pogg. Ann. **119**, 367 (1863).

coefficient of friction twenty three cases in which it seemed likely that an observed amplitude was not much greater than that at which the pulley would just begin to rotate. In three cases (18) gave negative values for the smaller tension. In the remaining twenty cases the calculated coefficients were of the same order of magnitude as the observed. In every case the calculated value was, as we should expect, somewhat larger than the observed, but in only one case was it as much as ten times as large. On the average the calculated values were about five times the observed. When we consider the data from which these results were obtained, the agreement is perhaps as good as could be expected.

Conclusion

On collecting the results of the three experimental tests of the theory for the rotation of the pulley we find: (1) That the general distribution of lengths of string for which the pulley actually rotated in a given sense tallies with the predictions of the theory only fairly; (2) that the values of the elastic modulus calculated from the lengths at which the rotation of the pulley reversed agree much better with the observed values; and (3) that the calculated values of the coefficient of friction between string and pulley, although very rough, probably agree with the observed values as well as could be expected.

I have pointed out that the sense in which the pulley rotates is not in all cases that which is predicted by the theory. In a considerable number of cases I have also found a reversal of rotation when the amplitude is sufficiently increased. In the present theory there is nothing to indicate any such reversal, and when comparing theoretical and experimental results I have aimed to use the rotation which occurred at the smaller amplitude.

When there are transverse vibrations of the string the theory will doubtless be more complicated. But before attempting to formulate that theory it would seem wise to see how the above theory is modified by taking into account the damping. It seems likely that the damping will modify the theory in such a way as to make the theoretical results agree more closely with those which are found experimentally. When this more extended theory has been developed and tested experimentally, it is entirely possible that the reversal of the sense of rotation of the pulley may provide a new means of studying the manner in which the elastic modulus of a cord or rope depends on the frequency with which the applied force changes.

Smith College,
November 24, 1925.

THE PHONIC WHEEL AND SURFACE TENSION OF LIQUIDS

By S. Ganapati Subramanyam

Abstract

A modification of Lord Rayleigh's stroboscopic method of measuring the velocity of ripples on the surface of liquids is described. A single, electromagnetically driven tuning fork is used to generate the ripples and at the same time to drive by means of a Rayleigh synchronous motor a stroboscopic disk having as many slots as there are teeth on the motor armature. When the liquid surface is viewed through the disk the ripples appear stationary and their wave-length may be measured. A sample set of data is presented giving a value of 73.7 dynes/cm for the surface tension of water at 30°C.

LORD RAYLEIGH was the first to apply the measurement of the velocity of propagation of ripples to the determination of surface tension. He generated the ripples by the motion of a glass plate which was attached to the lower prong of an electrically driven tuning fork and dipped into the liquid. When ripples travel over the surface of a liquid, their velocity is so great that they cannot be observed by the unaided eye. If these ripples are viewed by intermittent light, the frequency of the flashes of illumination being the same as that of the source of ripples, then in each interval a ripple will travel over one wave-length and will occupy the position occupied by the preceding ripple at the commencement of the interval. The ripples appear stationary. To obtain such intermittent glimpses of the surface, the surface is usually observed through the prongs of a second tuning fork of the same frequency and maintained in vibration by the same circuit. Thus two tuning forks are found necessary for the success of the experiment. Moreover their periods must be exactly determined. Lord Rayleigh in his experiments on greasy surfaces[1] used a pair of forks. The frequency of the interrupter was about 42 per second so that the intermittent current could be used to excite a fork of frequency about 126. The beats between this and a standard Koenig fork of frequency 128 were counted at intervals and found to be sufficiently constant.

A method involving the use of only one fork is described here. Water is placed in a large porcelain developing dish. To one prong of a tuning fork a thin piece of aluminum plate is attached and the latter dips into the water. The fork is driven electro-magnetically and the inter-

[1] Rayleigh, Scientific Papers, Vol. III, p. 387.

mittent electric current is made to drive a phonic wheel or Rayleigh synchronous motor. The phonic wheel consists of two electro-magnets and a rotating armature in the form of a soft iron wheel with 30 teeth. It was fitted with a permanent friction-wheel and was used with a stroboscopic disc having 30 slots. A timing attachment was arranged to ring a bell at every 100 revolutions of the motor spindle. The phonic wheel is made to run with its axis vertical. The porcelain dish is so placed underneath the stroboscopic disc that the surface of water in it is capable of being viewed through the slots in the disc. Thus the single fork acts the part of an interrupter as well as an exciter of ripples. An incandescent bulb was suspended about a metre and half above the surface of water, whose ripples then cast a series of shadows on the bottom of the white porcelain dish. Dividers are arranged also to cast a shadow and they are so adjusted that the two ends of the dividers' shadow coincide with the corresponding parts of the first and last number of waves that can be easily counted.

To start the motor it is speeded up by hand and then by proper manipulation kept rotating at approximately this speed until the position of the wheel becomes right and the motor falls in step with the interrupted currents from the fork. As the armature rotates, the magnetic circuit of the electromagnet is approximately closed whenever a pair of teeth are opposite the pole pieces. As there are 30 teeth in the armature, the circuit is closed 30 times during every revolution. The interval between any two closures of consecutive teeth is also the interval between the appearance in the field of view of any two consecutive slots in the disc and thus the ripples are seen by intermittent illumination, the frequency of the flashes of illumination being the same as that of the fork which excites the ripples.

The following is a sample set of observations on water at 30C. The mean time for 300 revolutions was 181.6 sec. Since there were 30 slots on the disk the time interval between flashes was .02016 sec. This as noted above is also the period, τ, of the fork, The dividers were set with their points 5 cm apart and there appeared between them 8.4 wavelets as viewed stroboscopically. This gave for the wave-length, λ, a value of 0.595 cm. The surface tension of the water may then be calculated by Rayleigh's formula

$$T=\frac{\lambda}{2\pi\tau}-\frac{g\lambda^2}{4\pi^2}$$

The value obtained is 73.7 dynes/cm.

ARTS COLLEGE,
RAJAMUNDRY, S. INDIA,
November 19, 1925.

BOOK REVIEWS

The Fundamental Concepts of Physics in the Light of Modern Discovery. PAUL R. HEYL.—This little book is a wholly admirable summary of the evolution of the leading physical theories of the present day. In simple language, within the comprehension of any educated reader, and with frequent enlivening touches of poetry and humor, it traces the development of the concepts of matter, heat, electricity and energy through the eighteenth and nineteenth centuries down to the startling advances of the past quarter-century. The foreword contains an eloquent appeal for a greater breadth of vision on the part of the scientific worker. "We physical scientists feel this most keenly, for modern thought presents to us concepts of a strange and bewildering nature, generalizations so broad as to strain our vision to include them in their entirety. We are gasping like our ancestor, the lung fish, in a dry season. And yet there are minds which have produced these concepts and laid out these generalizations; and there are many more who, while they cannot produce, are able to follow. The rest of us are confronted with the stern alternatives of keeping up with the procession or falling out."

In Chapter I we find an account of the development and decline of the caloric and phlogiston theories. The essentially materialistic character of the science of the period, combined with appeal to the supernatural when material explanations failed, is emphasized. Various respects in which the thought of the eighteenth century anticipated our modern theories are pointed out, for example the transformation of matter into radiation, the two-fluid theory of electricity, and potential energy. The second chapter recounts some of the chief discoveries of the nineteenth century. Among the achievements of this century are discussed especially the growth of the concept of energy and the correlation of the scattered ideas of the century preceding. Excellent perspective views are given of Mayer's first determination of the mechanical equivalent, and of the principle of the conservation of energy. Unusually clear expositions of the second law of thermodynamics and its limitations, and of entropy, are given, ending with the following bit of wisdom: "Nothing, to the popular mind, can be less akin than poetry and mathematics; and the concept to which we refer, that of entropy, is abstract and mathematical to a high degree, being defined by an integral, and not capable of being as readily visualized as its sister concept of energy. Nevertheless there may be such a thing as poetry under an integral sign, incongruous as the association may appear." Comparatively little space is devoted to Maxwell's great contributions. The final chapter, on the twentieth century, or the "Century of Hope," occupies nearly half of the book. The author constantly points out the evolution of present ideas from those of the past, as well as the need of further advancement into the unknown. The outstanding features of this chapter are the accounts of the modern theory of matter, including the quantum theory, and relativity. With great clarity Einstein's deductions of the correlation of gravity and inertia, and of the relation between matter and energy, are described, and the difficulties in the way of experimental verification are noted. These pages on relativity and its shortcomings contain the best popular exposition of the subject that we have yet seen. Unfortunately the book was written just too early for a consideration of Miller's latest experiments on ether drift.

A good list of references to original memoirs is provided. Nevertheless one cannot help wishing that the author had been more explicit as regards dates of discoveries and the names of those to whom some of the advances are due. As to errors, it is perhaps unfair to expect rigorous exactness in a book for popular reading, yet the statement on page 73, that the quantum concept "atomizes energy into indivisible units, not all of

the same size, but integral multiples of the smallest of them," without mention of the effect of frequency, seems needlessly misleading, likewise the statement on page 83, that "the magnetic attraction can be cut off by a suitable screen." The book concludes with a consideration of the attitude of the scientist toward the future. The following quotation is typical of the picturesque style of the book: "The physicist, above all others, remembers how Galileo invited the learned men of his day to look through his telescope and how they refused to do so; but he also remembers how the Pilgrim made his progress through Vanity Fair, urged ceaselessly on all sides to buy this, that or the other brilliant trinket, and how he held steadfastly to his way, clutching to his bosom that which had proved itself to be his only safe guide through all the perils of the way he had come." Pp. xii+112. Williams & Wilkins Company, Baltimore, 1926. Price $2.00.

WALTER G. CADY

A Textbook of Physics. (Third edition). L. B. SPINNEY.—The former editions of this book have won for themselves a place among the best American college texts on physics, and this high level promises to be maintained by the third edition. The book is distinguished by its clarity of statement, excellent figures, and well selected numerical examples. While the latter are for the most part the same as in the second edition, still in many cases numerical values have been altered and some new examples have been added. Inasmuch as some acquaintance with trigonometry is assumed, trigonometrical expressions might well have been introduced more freely, especially in the resolution of forces in the chapters on statics and on magnetism. The judicious emphasis placed upon the more essential facts and principles is an excellent feature; but the revision of some of the chapters, particularly with respect to such topics as radio telegraphy and modern atomic theory, could have been more thorough. While realizing that this is a matter of opinion, the reviewer cannot refrain from pointing out certain matters that have been either omitted or rather scantily treated. These are, for example, shear and rigidity; self and mutual inductance, and the transformer; the ear; fluorescence and phosphorescence; the Foucault pendulum; photo-electricity and quanta. Thermo-electricity is hardly mentioned. Excellent historical notes are given here and there, but the name of Röntgen appears only in the index, and there is no mention, in the paragraphs on atomic structure, of the chief names concerned with its modern development. On pages 443, 444 we read that the proton "has always the same mass," and that protons and electrons "appear to be equal in diameter." As in too many textbooks, the correct explanation of the part played by the dielectric in the phenomenon of residual charge and in the experiment with the "dissectable jar" is not given. As we have stated, these criticisms are largely a matter of opinion. In the main, Professor Spinney has covered the field with a degree of care and completeness that makes the book distinctly to be recommended.—Pp. xiii+635, 420 figs. The Macmillan Company, New York, 1925.

WALTER G. CADY

Die Neuere Entwicklung der Quantentheorie. Second Edition.—A. LANDÉ (Wissenschaftliche Forschungsberichte, Band V)—The new edition of this book indeed merits the statement that it is "fully revised", for it is twice the length of the first edition (which carried the somewhat different title "Fortschritte der Quantentheorie"). A large number of diverse subjects are summarized, including multiplet structures and the anomalous Zeeman effect, specific heats, the mechanics of the hydrogen atom, and the quantization of perturbed systems by Bohr's method of variation of constants. Einstein's recent work on the degradation of gases is very properly presented in greater detail than many of the other more familiar subjects. In discussing chemical constants and spectroscopic magneton numbers, the author glosses over apparent experimental contradictions, probably because the book does not in general include extensive comparisons with experiment. The first chapter, which is entirely new, is devoted to the structure of radiation.

Here both corpuscular light-quants and virtual oscillators are presented as helpful concepts.

The book does not purport to be a complete text, but instead, to quote the author, is intended for "readers who are content with a brief recapitulation of the elements of the quantum theory." The aims of a good syllabus are fulfilled, for the subject matter is usually well chosen and accurately presented. The style is of necessity a condensed one, and this may make certain chapters rather difficult for readers not already familiar with the quantum theory.

An index is included, and also a bibliography in which over 300 papers are listed. Consequently the book is well worth having for reference purposes. The bibliography is fairly complete in its listing of German papers, but certainly the opposite for those in English. References, for instance, are given to the work of Fues, Schrödinger, van Urk, and Wentzel on atomic force fields, but there is no mention of the contributions of Hartree and Lindsay. Several other omissions of like nature could also be cited. The correlation of text and bibliography is poor. Important contributions mentioned in the text are not listed at all in the bibliography (as, for instance, the recent work of Compton and Simon on scattered light-quants), while the bibliography contains numerous papers without any very obvious relation to the text-material, though this is obscured by the unfortunate omission of the titles of papers. The bibliography on the correspondence principle, for instance, contains a miscellaneous, incomplete assortment of papers on the polarization of resonance radiation. The theory of specific heats is presented in the text after the early Ehrenfest method, but bibliography references are given to the more satisfactory Reiche theory with, of course, no mention of American contributions.

One must indeed admire the celerity with which the book has been printed, for it is ready for distribution only two months later than the date of writing. Consequently, the references to the German papers are up-to-the-minute, including even a section on matrix dynamics. In view of the obvious speed of writing, one can perhaps excuse the occasional misspelled names in the bibliography.—Pp. xi+180, 14 fig, Steinkopff, 1926. 12 marks; bound, 13.20.

J. H. Van Vleck

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

Minutes of the Stanford Meeting, March 6, 1926.

The 138th meeting of the American Physical Society was held at Stanford University on March 6, 1926. Professor Fernando Sanford presided. Morning and afternoon sessions were held with an attendance of about eighty. The Society held an informal luncheon at the Stanford Union, attended by fifty-five members and guests.

The regular scientific session consisted of 27 papers, (one of which was read by title) abstracts of which are given on the following pages. An **Author Index** will be found at the end.

DAVID L. WEBSTER,
Local Secretary for the Pacific Coast.

ABSTRACTS OF PAPERS

1. The Compton effect and virtual oscillators. P. A. Ross, Stanford University.—In recent papers by Slater and by Bohr, Kramers, and Slater an attempt has been made to reconcile quantum theory and wave theory by postulating certain "virtual oscillators" which shall be capable of absorbing waves to synthesize quanta. If such virtual oscillators were in a region illuminated by monochromatic radiation from two sources of the same frequency it would seem reasonable that the oscillator should build up its quanta by absorbing radiation from both sources and thus acquire momentum along the resultant Poynting vector. If this absorbed quantum were passed over to an electron to be scattered according to the Compton equation, the angle of scattering and consequent change of wave-length should correspond, not to the angle between the scattered beam and either incident radiation, but to the angle between the scattered beam and the resultant Poynting vector. This was tested by placing a graphite scattering block between two x-ray tubes driven in parallel from the same transformer. Two spectrographs were set up. One received radiation scattered at 90° to both incident beams. The other received radiation at angles of 125° and 55°, respectively, from the two beams. The normal Compton effect was observed. The above theory would demand no shift.

2. The Doppler principle and the quantum hypothesis. G. E. M. JAUNCEY, Washington University.—The relativity theory demands that when an atom at rest changes from an energy state W_1 to an energy state W_2 there is a change of mass from M_1 to M_2. Hence emission of radiation is accompanied by loss of mass. Suppose an atom of mass M_1 moving with velocity $\beta_1 c$ emits a quantum in the forward direction, after which the atom has a mass M_2 and velocity $\beta_2 c$. Conservation of energy requires $M_1c^2/\sqrt{1-\beta_1^2}=h\nu+M_2c^2/\sqrt{1-\beta_2^2}$, while conservation of momentum requires $M_1\beta_1 c/\sqrt{1-\beta_1^2}=h\nu/c+M_2\beta_2 c/\sqrt{1-\beta_2^2}$. Eliminating β_2 and solving for ν, we obtain ν as a function of β_1. Now calling ν_0 the value of ν when $\beta_1=0$, we obtain $\nu/\nu_0=(1+\beta_1)/\sqrt{1-\beta_1^2}$. If β_1 is small and we put $\beta_1 c=v$, then $\nu/\nu_0=(c+v)/c$. The formula for the Doppler principle has thus been obtained without the use of the classical wave-theory.

3. The continuity of the x-ray spectrum at a wave-length twice the short-wave limit. D. L. WEBSTER, Stanford University.—Planck's theory of heat radiation indicated a probability that an oscillator might emit any integral number of quanta at once, the probability of a number greater than one being greatest under conditions giving most rapid absorption. Since the absorption of energy from a cathode ray is presumably very rapid, one might expect double-quantum emission in x-rays. Evidence for this would appear in the continuous spectrum as a discontinuity of slope at twice the short-wave limit. Discontinuities of this sort in observed spectra have been interpreted as second-orders of the short-wave limit, and Kirkpatrick verified this interpretation, approximately, by absorption tests. The need for such means of eliminating second orders practically vanishes with the use of diamond, in which Bragg found the second order very faint. In work on the use of diamond for spectral intensity measurements, the author has tested the continuity of spectra and isochromats of tungsten, finding no evidence of any double-quantum radiation. The change of slope of an isochromat at twice the excitation voltage, if it exists at all, is not over a very few percent of that at the excitation voltage itself.

4. The crystal structure of $[N(CH_3)_4]_2PtCl_6$. MAURICE L. HUGGINS, Stanford University.—Using Laue and spectrum photographs and the theory of space groups, the structure of tetramethyl-ammonium chloroplatinate has been determined. The structure has cubic symmetry, with $a_0=12.65$A. Pt and N atoms are disposed as are the Ca and F atoms in CaF_2 (special cases 4*b* and 8*e* in Wyckoff's "The Analytical Expression of the Results of the Theory of Space-Groups"). Each Pt is surrounded by 6 Cl atoms (24*a*) at corners of a regular octahedron, and each N is surrounded by four C atoms (32*a*) at corners of a regular tetrahedron. The symmetry is that of the space-group $O_h^5(Oi-5)$ or that of $O^3(O-3)$. Assuming the N–C distance to be 1.47A, the best agreement with the data is obtained when Pt–Cl is taken as about 2.35A. This research was done while the author was National Research Fellow in Chemistry at the California Institute of Technology.

5. The crystal structures of anatase and rutile, the tetragonal forms of TiO_2. MAURICE L. HUGGINS, Stanford University.—Using Laue and spectrum photographs and the theory of space-groups, the structure obtained by Vegard for anatase and that obtained by Vegard and by Greenwood for rutile have been verified. The unit cell of anatase has the dimensions $a_0=3.78$A and $c_0=9.50$A; it contains Ti atoms at (000) $(0,\frac{1}{2},\frac{1}{4})(\frac{1}{2},0,\frac{3}{4})(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and O atoms at $(00u)(0,\frac{1}{2},u+\frac{1}{4})(\frac{1}{2},0,u+\frac{3}{4})(\frac{1}{2},\frac{1}{2},u+\frac{1}{2})(00\bar{u})(0,\frac{1}{2},\frac{1}{4}-u)$ $(\frac{1}{2},0,\frac{3}{4}-u)(\frac{1}{2},\frac{1}{2},\frac{1}{2}-u)$ where $u=.20\pm.01$. The symmetry of this arrangement is that of the space group $D_{4h}^{19}(4Di-19)$. For rutile $a_0=4.58$A and $c_0=2.95$A; Ti atoms are in the positions $(000)(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and O in $(uuo)(\bar{u}\bar{u}o)(\frac{1}{2}-u,u+\frac{1}{2},\frac{1}{2})(u+\frac{1}{2},\frac{1}{2}-u,\frac{1}{2})$, where $u=.30$ $\pm.01$. The symmetry is that of $D_{4h}^{14}(4\ Di-14)$. This research was done while the author was National Research Fellow in Chemistry at the California Institute of Technology.

6. PP′ groups in the elements S(I) to K(IV). J. J. HOPFIELD and G. H. DIEKE, University of California.—Two new *PP′* multiplets representing double electronic transitions in A (III) and K (IV) have been added to those already observed (Hopfield, Phys. Rev. **23**, 766 and **26**, 282). The final state of these four groups is the lowest *P* level, which is also the valence level. The six lines of these multiplets are clearly resolved on our spectrograms of S, Cl and A. The position of the multiplet in K(IV) was predicted and then found among Millikan and Bowen's data. The wave numbers of the multiplets are: S(I), 72380, 72174, 72019, 71985, 71805, 71625; Cl (II), 93995, 93626, 93357, 93305, 92995, 92669; A(III), 114797, 114216, 113803, 113687, 113228, 112690; K (IV), 135691, 134745, 134174, 133326, 132222. Bowen and Millikan (Phys. Rev. **26**, 150) have also observed *PP′* groups in a series of elements. A comparison of this work with their's shows (1) that the structures of the groups are alike except that in the present case the

triple levels are inverted, (2) that the successive frequency differences of the groups S (I) to K (IV) are nearly equal to those of Mg (I) to Cl (VI), (3) that the difference in frequency between the S (I) and the S (V) multiplets is approximately equal to the separation of the Cl (II) and the Cl (VI) groups. This multiplet has not been found in O (I).

7. Series due to halogens in infra-red absorption spectra of organic compounds. JOSEPH W. ELLIS, University of California, Southern Branch.—Absorption band series, attributed to carbon-hydrogen and carbon-carbon bonds have previously been reported by the writer. The absorption spectra of methylene chloride and chloroform contain, in addition to the C-H series, bands which fit a linear, or "harmonic," series whose initial wave-length member seems to be 16.8μ. The remaining bands of the short wave-length spectra can readily be accounted for by combinations between this series and the C-H series. Similarly, bands in the spectra of methylene bromide and bromoform, and methyl iodide and methylene iodide, can be grouped into linear series, which start at 17.2μ and 17.5μ, respectively. Members of combination series can also be identified in these latter spectra. Members of these series can also be found in spectra of more complicated molecules containing halogen atoms, but the spectra are complicated by the presence of bands due to C-C pairs. That these bands are due to the presence of halogen atoms seems certain; that the presence of hydrogen in the molecule is necessary for their appearance seems also certain, as carbon tetrachloride and tetrachlorethylene, containing only carbon and chlorine atoms, show no absorption in the short wave infra-red region.

8. On the specific heat of hydrogen. G. H. DIEKE, University of California.—A recalculation of the specific heat of hydrogen has been made on the basis of the new development in band spectra. The *probabilities a priori* have to be of the form $p_j = j + a$, where a can be left undetermined. (j is the total moment of momentum of the molecule.) The results are: (a) m (rotational quantum number) $= \frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, \ldots$. Only moderate agreement between theory and observations for any choice of the p_j; (b) $m = 1\frac{1}{2}, 2\frac{1}{2}, 3\frac{1}{2}, \ldots$. (suggested by the visible H_2 bands (Fulcher bands). (Dieke, Proc. Amsterdam, **27**, 490. See also Hutchisson and Van Vleck, Phys. Rev. **25**, 243) gives much better results with the p_j to be expected by theory; (c) $m = j \pm \frac{1}{2}$, which is suggested by the alternating intensities in the Fulcher bands gives also good agreement for low temperatures. Other assumptions, less probable, also give curves which agree fairly well at low temperatures. The present measurements are not sufficient to decide in favor of one particular hypothesis. For higher temperatures the non-rigidity of the molecule would change the curves considerably. There are, however, no data as yet which would allow with any certainty the calculation of the curves for a non-rigid molecule.

9. New oxygen bands between λ2000–2300. VIVIAN M. ELLSWORTH and J. J. HOPFIELD, University of California.—Sixteen new bands due to ionized oxygen have been photographed in the region 2000–2300. They occur in pairs degraded to the red. The pairs have a constant frequency difference of 200 units. The bands appear to be an extension to the ultra-violet of the group of electronic O_2^+ bands arranged in Deslandres progressions by Johnson. Mecke and Birge made quantum assignments of the group. The progression having the lowest final state according to Mecke's interpretation, is now extended by two members having higher initial states than those previously reported. The total number of initial states now indicated is ten. A new progression having a still lower final state appears and fits the scheme. This necessitates raising the previously assigned quantum numbers for the final states by at least one unit. Other bands which are too dim to measure but which have the characteristic appearance of the group and may belong to it, appear farther to the ultraviolet. The 0,0 band and those in its neighborhood are still missing and the general character of the schematic arrangement is unchanged by the additions.

10. On the absorption bands of nitric oxide. H. SPONER and J. J. HOPFIELD, University of California.—It was recently shown by one of us that the final state of the third positive group of nitrogen (γ bands) is the stable state of NO. Now it was found from absorption plates in NO taken by Dr. Leifson and kindly sent to us, that also the β bands occur on these plates proving that the β and the third group bands have a common final state as was suggested by Mulliken and by Birge. This progression from the normal state extends the scheme of the β bands from $n''=3$ (final) to $n''=0$ ($n'=2$ to 5 initial). According to a suggestion by Mulliken, the stable state is a double p level corresponding to aluminum, while the initial state of the third positive group bands corresponds to an s level and that of the β bands to a double d level.

11. The fine structure of the λ4842 band of AlO. WILLIAM C. POMEROY, University of California.—The rotational energy of the AlO molecule has been represented by $F=Bm^2+Dm^4+Fm^6+Hm^8$ where $m=k-\epsilon$. k is a half integer representing the resultant molecular momentum. Approximate values of ϵ are .0074 and .01 for the initial and final states respectively. Vibrational frequencies for infinitesimal vibration calculated from Kratzer's formula, $\omega=\sqrt{-4B^3/D}$, agree with values obtained from vibration data alone within 0.2%. The doublet separation of band lines was represented as a function of k of the initial state for both the P and R branches by a single equation, $\Delta\nu=.0116k+12\times10^{-6}k^2-7\times10^{-11}k^4$. Attributing the doublets to a double energy level in the initial state $(F')^{+-}=(.6019\pm6\times10^{-6})m^2-(1.1630\times10^{-6}\pm3.5\times10^{-11})m^4+.54\times10^{-12}m^6$ where $m=k-0.0074\pm0.00482$; $(F'')=.6386m^2-1.1094\times10^{-6}m^4-.43\times10^{-12}m^6-5.2\times10^{-18}m^8$. Throughout the measured range ($k=140.5$), observed frequencies of lines of the (0,0) band agree with those calculated from $P_k{}^{+-}=20635.27+(F'_{k-1})^{+-}-F_k''$; $R_k{}^{+-}=20635.27+(F'_{k-1})^{+-}-F_k''$ with residuals rarely exceeding .04 cm^{-1} (.01A).

12. Theory of intensity distribution in band systems. EDWARD CONDON, University of California.—Franck (Trans. Faraday Soc. 1925) has given a simple mechanical explanation for the large change in vibration quantum number in the absorption bands of cold (non-vibrating) iodine molecules. It is assumed that the electron transition affects only the binding of the atoms, leaving unaltered the relative nuclear separation. Quantitative treatment of this model by the author embodies the application to transitions where the molecule is vibrating in the initial state and assumes further that the nuclear velocities are not changed by the electron transition, explaining thereby the major aspects of the observed intensity distributions in band systems in emission and absorption. The theoretical expression is: $n''=\pi\omega''md^2/h+\frac{1}{2}(\omega'/\omega''+\omega''/\omega')n'-\sqrt{n_i}\sqrt{4\omega''/\omega'(\pi\omega''md^2/h)}\sin\theta+\frac{1}{2}(\omega'/\omega''-\omega''/\omega')n'\cos2\theta$. Here n'' and n' are the final and initial vibration quantum numbers, ω'' and ω' the final and initial vibration frequencies, m the reduced mass, d the difference in equilibrium separation in the two electronic states and θ the phase of the vibration at the instant of electron transition. Applied to the meager experimental data for emission bands of AlO, CO, CO^+, N_2 (2nd pos. group), $N_2{}^+$ (1st neg. group), SiN and I_2 the theory is in good accord with the facts.

13. The heat of dissociation of non-polar molecules, as determined from band spectra, and from other sources. RAYMOND T. BIRGE and HERTHA SPONER, University of California.—The limiting amount of vibrational energy which a diatomic molecule can possess is given by $E_n=h\int_0^{n_0}\omega^n dn$, where ω^n is the frequency of vibration, as a function of the vibrational quantum number n, and n_0 is the value of n for $\omega^n=0$. For *non-polar* molecules n_0 is finite, for polar molecules it is infinite. Usually the ω^n:n curve for the stable molecular state is strictly linear, over the known range, and its linear extrapolation to $\omega^n=0$, *for essentially non-polar molecules*, seems to give the true value of E_n to within half a volt. Since the molecule dissociates into two stable atoms, $E_n=Q$, the heat of dissociation. When the molecule dissociates, while excited by E_n units of

electronic energy, the products of dissociation seem from previous work on iodine to be one stable and one excited atom (of excitation energy A). Hence $Q+A=E_s+E_n$. For dissociation from certain excited states of O_2, CO, and NO, A seems to be negligible (see following abstracts). Values of Q have thus been obtained for O_2, O_2^+, N_2, N_2^+, CO, CO^+, and NO. These values are self-consistent and are also consistent with data from other sources.

14. The heat of dissociation of O_2 and O_2^+. RAYMOND T. BIRGE, University of California.—Using new data by Hopfield and Leifson, the ω^n:n curve for the excited state of the Schumann bands of oxygen is known almost to $\omega^n=0$. The true value of E_n (see preceding abstract) is thus known to ± 0.01 volt. $E_s+E_n(=Q+A)=7.05$ volts, and A is probably only 0.01 or 0.03 volts. (The stable state of oxygen atom is a triple p level, of 0.01 and 0.02 volts spacing.) Hence the true heat of dissociation of O_2 is 7.05 ± 0.03 volts. Mulliken finds that the Runge bands are a portion of the above system, and the new data thus available for the stable state of O_2 yield an apparently linear ω^n:n curve from $n=0$ to 17. Its linear extrapolation (to $n_s=69$) gives $E_n=Q=6.66$ volts, showing the probable error (± 0.5 volts) of such an extrapolation. The O_2^+ bands give $Q'=6.46$ volts, from a linear ω^n:n curve for the stable state, and 6.49 volts from a linear excited state curve, ($O_2^+ + Q'$ volts $= O+O^+$). I' (ionization potential of atom) $=13.54$ volts. Therefore I (ionization potential of molecule) $=14.1$ volts, since from conservation of energy, $I+Q'=Q+I'$, always. These values agree with the Hogness and Lunn results of positive ray analysis of oxygen.

15. The heat of dissociation of N_2 and N_2^+. HERTHA SPONER, University of California.—Q for N_2 has been suggested by the writer as about 11.4 volts, from the energy of active nitrogen. The ω^n data for the stable state are unknown. The ω^n:n curve for the final state of the first positive group gives $E_s+E_n=8.0+3.87=11.87$ volts. Because of the non-linear character of the curve, this result is only approximate. The above value is supported by the results of Hogness and Lunn, who get N^+ ions at 24 volts has the result of a collision of an excited N_2 with a neutral molecule. The explanation can be given by the process N_2^{exc} (24)$\rightarrow$N+N$^+$(13–14)$+Q$(11.4). The value for ionization of N(=13–14) is estimated roughly from spectroscopic data. For N_2^+ one obtains 9.06 volts for Q' from a linear graph for the final state, and 9.7 volts from the linear extrapolation of an actual negatively curved ω^n:n graph. Hence this last result should be too large. Using the $I+Q'=Q+I'$ equation with the known $I=16.5$ volts, $16.5+9.06=11.4+I'$. This gives $I'=14.16$ volts, to be compared with the above 13–14 volts. The agreement is within the limits of error.

16. The heat of dissociation of CO, CO^+, and NO. RAYMOND T. BIRGE and HERTHA SPONER, University of California.—A strictly linear ω^n:n curve for the stable state of CO (known to $n=22$) gives $Q=11.18$ volts. The next higher electronic level gives $Q=12$ volts, but is more uncertain. The third level is unsuitable for this work. The heat of sublimation of diamond (6.11 volts) and other known chemical data, combined with the now known value $Q=7.05$ volts for O_2, give $Q=10.78$ volts for CO, a probably better value than 11.18. Only the stable state of CO^+ gives a linear ω^n:n curve and the resulting $Q'=9.82$ volts, ($CO^+ + Q'$ volts $= C+O^+$ assumed). The known I for CO is 14.2 volts, and I' (of oxygen atom) is 13.5 volts. Hence $I+Q'=Q+I'$ becomes $14.2+9.82=10.78+13.5$, a satisfactory agreement. For NO only the excited state of the gamma bands gives a linear ω^n:n curve. The resulting $E_s+E_n=17.19$ volts. Assuming $Q=7.05$ for O_2 and 11.4 for N_2, and knowing $N_2+O_2+1.9$ volts $=2$ NO, $Q=8.27$ volts for NO. Since $E_s+E_n=Q+A$, A equals 8.92 volts, and this type of dissociation of NO seemingly results in a neutral nitrogen and an 8.9 volt excited oxygen atom, agreeing with the known resonance potential of oxygen (9.1 volts).

17. Rate of neutralization of the field in the Braun tube with external electrodes. A. M. CRAVATH and L. T. JONES, University of California.—This is a study of a problem

which arose in the investigations of Jones and Tasker, J.O.S.A., 9, 471, 1924. The field of the external electrodes is rapidly neutralized by the collection of ions and electrons on the tube walls, so that the deflection is not proportional simply to the applied voltage. The neutralization proceeds like the discharge of a condenser with time constant $RC=\tau$. This time constant τ, which is a reciprocal measure of the rate of neutralization, was calculated from current measurements made with internal electrodes, and was measured directly by photographing the variation of deflection with time, the two values for the tube used being 0.002 and 0.0013 seconds. From the latter value it is calculated that for sinusoidal voltages of 60 and 7000 cycles per second the deflection should lead the applied voltage by 65° and 1° and the amplitudes should be reduced to 40% and 99.98% of the values they would have in the absence of neutralization.

18. Phase and magnitude of deflections of Braun tube beam with internal and external electrodes. R. A. JACK and L. T. JONES, University of California.—Photographs showing a 90° phase difference between the deflections of a cathode beam of a Braun tube with 60 cycle alternating potential applied to external and internal electrodes, respectively, were published by Jones and Tasker. (J.O.S.A. 9, 471, 1924; Phys. Rev. 23, 777, 1924). The following work has been done to determine the phase difference at different frequencies and to determine the deflection as a function of frequency with external electrodes. At the lower frequencies the deflection is a function of the frequency, while at the higher range the deflection becomes constant. At high frequencies the deflections with external and internal electrodes are apparently equal. By the use of Lissajous' figures, with the internal and external sets of electrodes at right angles, the phase difference has been found to disappear at high frequencies. Work is being continued to complete the frequency range from 60 to several million cycles.

19. The ionization of oxygen as interpreted by positive ray analysis. T. R. HOGNESS and E. G. LUNN, University of California.—Positive-ray analysis of the products of electron-impact ionization in oxygen shows that the percentage of the ions, O_1^+ and O_2^+ is independent of the pressure of oxygen. Evidence is thus given that O_1^+ and O_2^+ are formed by independent processes, and hence that an impact electron can dissociate oxygen with the formation of the atomic ion. The ionization potentials for the formation of O_2^+ and O_1^+ were found to be 13 and 20 volts, respectively. The latter, together with Hopfield's series limit, gives 6.5 volts (150,000 calories) for the heat of dissociation of oxygen.

20. Mobilities of gas ions in HCl. LEONARD B. LOEB, University of California.—Mobility measurements were made in pure dry HCl gas using the Franck modification of the Rutherford method with an alternating potential of square wave form. The average mobility for the positive ion at 20°C and 760 mm was found to be 0.65 cm/sec per volt/cm and 0.56 cm/sec per volt/cm for the negative ion. This measurement of a negative mobility definitely less than a positive mobility constitutes the first exception to a general rule previously assumed from observation which indicated that the negative ion had a mobility either equal to or greater than the positive ion, *but not less*. The inverse pressure law of mobilities was found to hold for both positive and negative ions down to 16.3 mm pressure. It was concluded from this that the constant of attachment of electrons to HCl molecules to form negative ions was nearly as low as that for Cl_2 gas. Finally, measurements of mobilities in mixtures of air and HCl showed unmistakable signs of a cluster ion formation in this gas, the mobilities being lowered by marked amounts for fractions of a percent of HCl gas.

21. On the theory of electrolytes. F. ZWICKY, California Institute of Technology.—The theory of Arrhenius accounted for the different properties of electrolytic solutions with the hypothesis of complete or partial dissociation of the molecules of the solute, the degree of dissociation being a function of the concentration. After it had been shown,

that for strong electrolytes the dissociation is complete at all concentrations, another explanation for the behavior of such solutions had to be found. Concerning the osmotic equation of state and the electrical conductivity, the problem was solved by Milner and Debye in introducing the so-called "ion-atmospheres." The ordinary equation of state (thermal and caloric), however, has not yet been treated and it is now proposed to deduce it in a general way. It appears that the effects due to the electric charges of the ions are predominant. These effects are, in outline, the following: (1) formation of ion-atmospheres; (2) electric polarization of the solvent; (3) attraction of the molecules of the solvent towards the ions with resulting high pressures (as great as 50000 atm.) in the vicinity of the ions. The mathematical treatment of these effects gives results, which are in complete agreement with the observed data of specific heat, compressibility, thermal coefficient of expansion and volume-contraction on solution.

22. Variations in Hall effect and thermoelectric power due to changes in crystallinity. L. J. NEUMAN, University of California.—Variations of the Hall constant due to changes in crystallinity have been investigated. Strain-hardening was found to produce an increase in R for Bi from -5.78 to -9.27. In Sn and Cu, however, the value of R is decreased by similar treatment. Thermoelectric effects between specimens of Fe, All Ni, Zn, Cu, Au, and german silver possessing different degrees of crystallinity have been measured for temperatures from 0°C to 1000°C. Thermoelectric powers of over 2 microvolts per degree C have been observed between annealed and strain-hardened specimens of a single metal. The sign of the e.m.f. is the same for all of the metals investigated. Thermoelectric effects between single capillary crystals are discussed and data given.

23. Errors in measurement of the Thomson effect and an anomalous effect in Bismuth. MARCUS O'DAY, University of California.—Especial care must be taken in the measurement of the Thomson Effect that there is no chance for leakage of the main current to the measuring apparatus. Experiments conducted by the writer have shown that with ordinary precautions against leaks, a small stray current to the measuring apparatus would behave just as a normal Thomson Effect if thermocouples are used for the measurement of temperature. Using extreme precautions against this and isolating the thermocouples in pyrex glass tubes the writer has worked on the effect in bismuth using heavy currents. Several thermocouples were placed along the bar and the change of temperature measured upon reversal of the main current. However, instead of the change of temperature being proportional to the temperature gradient, the writer finds a direct proportionality to the temperature. It is suggested that this may be due perhaps to an asymmetrical thermal conductivity due to the method by which the bars were cast. It was found upon examination of the crystals in the bars that due to the expansion of bismuth upon solidifying the center of the bar is displaced upward forming a very peculiar funnel-shaped crystal.

24. Performance of the graphic acoustic sounder during the Australian cruise of the U. S. fleet. L. P. DELSASSO, University of California, Southern Branch.—By authorization of the Bureau of Engineering of the Navy Department, the device reported at a previous meeting was installed aboard the U. S. S. Maryland. Wherever the position of the ship could be fixed accurately it was found that the record obtained with the Graphic Acoustic Sounder was in good agreement with the charted depth. The device was found to operate satisfactorily from 20 to 3500 fathoms. It is shown that the shallow limit is fixed by the oscillator characteristics, while the maximum depth may be extended by the use of filters and greater amplification.

25. Measurement of reverberation with the thermionic tube oscillator. VERN O. KNUDSEN, University of California, Southern Branch.—The writer has made reverberation measurements, using an audio-frequency oscillator and a high quality loud speaking telephone receiver instead of a series of organ pipes as has been used by W. C. Sabine

and other investigators. The arrangement has the following advantages: (1) The acoustic energy generated by the receiver is proportional to the electric energy actuating the receiver, and therefore test tones of standard intensity are readily obtained from simple measurements of currents and impedances; (2) each standard test tone is based upon its tone of minimal audibility, the latter being determined by taking many measurements in different parts of the room, and therefore the reverberation measurements are almost independent of slight residual noises in a room, and do not require correction for the volume and absorption of the room; (3) the apparatus is more portable and convenient than the organ pipes with their auxiliary equipment. The apparatus has been used satisfactorily to determine the coefficients of sound absorption of many new materials used for the reduction of reverberation and noise in architectural interiors.

26. An application of the Quantum Theory to the luminosity of diffuse nebulae. H. ZANSTRA, National Research Fellow, California Institute of Technology.—It is well established, that galactic nebulae are emitting light under the influence of neighboring stars. Approximating the star by a black body and the nebula by a mass of pure hydrogen the following mechanism is worked out for the production of the nebular hydrogen spectrum. The ultraviolet star light beyond the head of the Lyman series is completely absorbed, causing ionization of the nebular atoms. The subsequent re-combination causes the re-emission of line spectra and continuous spectra. To account for the photographic intensity of the observed nebular emission spectrum produced under the influence of stars B_0 and Oe_5 (Hubble), we have to assign a temperature to those stars of about 33000°. This value is sufficiently close to temperature estimates from other sources (thermal ionisation). Further work is in progress, including a more refined temperature determination from the observed luminosity for the stars B_0 and Oe_5, and an application to planetary nebulae.

27. Remarks on penetrating radiation. EDWARD CONDON, University of California.—An atomic model for Rutherford's "neutron" is presented which has an oscillation frequency closely corresponding to that estimated by Millikan from his recent measurements of the absorption coefficient of the radiation. A correction to the method of reducing the observations indicates that the absorption coefficient may be but half that given by the usual exponential law. The model used considers the oscillation of a proton inside an electron which has a volume distribution of electricity. The agreement of the frequencies observed and computed, is better than a 10% discrepancy.

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